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PROJECT ADMINISTRATION DATA SHEET

[X] ORIGINAL [ ] REVISION NO. ______

Project No. G-35-642 (R5999-0A0) GTRC/~~GIT~~ DATE 8 / 16 / 85

Project Director: Dr. E. Michael Perdue School/~~Lab~~ Geophysical Sciences

Sponsor: Southern Company Services, Inc.

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Title: The Contribution of Leachable Organic Acids in Forest Soils to the Acidification of Surface Waters

ADMINISTRATIVE DATA

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Defense Priority Rating: N/A

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(or) Company/Industrial Proprietary: See Below

RESTRICTIONS

See Attached N/A Supplemental Information Sheet for Additional Requirements.

Travel: Foreign travel must have prior approval – Contact OCA in each case. Domestic travel requires sponsor approval where total will exceed greater of $500 or 125% of approved proposal budget category.

Equipment: Title vests with Sponsor

COMMENTS:

A Non-Disclosure Agreement has been negotiated.

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Project Director	Procurement/EES Supply Services	GTRC
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Accounting	Research Communications (2)	Other Jones

FORM OCA 65:285

GEORGIA INSTITUTE OF TECHNOLOGY
OFFICE OF CONTRACT ADMINISTRATION

NOTICE OF PROJECT CLOSEOUT

Closeout Notice Date 02/02/90

Project No. G-35-642 Center No. R5999-0A0

Project Director PERDUE E M School/Lab E & A SCI

Sponsor SOUTHERN COMPANY SERVICES/

Contract/Grant No. 195-84-025 Contract Entity GTRC

Prime Contract No.

Title CONTRIBUTION LEACHABLE ORGANIC ACIDS FOREST SOILS ACIDIFICATION SURFACE W

Effective Completion Date 870401 (Performance) 870401 (Reports)

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Comments

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Distribution Required:

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NOTE: Final Patent Questionnaire sent to PDPI.

G-35-642

The Contribution of Leachable Organic Acids in Forest Soils to the Acidification of Surface Waters

Letter Report No. 1 - Submitted on November 15, 1985

by E. M. Perdue and R. W. Garber

Samples (approximately 2 kg) of forest soil litter (upper 1 cm) were collected from two sites in the Raven Fork watershed in the Great Smoky Mountain National Park. A red spruce site and a northern hardwoods site, both of which are being used for related TVA watershed research studies, were selected for this study.

All samples were collected in clean polyethylene bags, which were placed in burlap bags to prevent physical damage during horseback transport out of the watershed. Samples were stored under ice for transport to the laboratory and then transferred to a laboratory refrigerator (at 3 C).

Litter samples (20 g) from each site were leached with deionized water (20 mL). The resulting leachate solutions contained significant free acidity and were particularly rich in undissociated acids (those titratable up to pH 10.5).

	Leachate Solutions		
Forest Litter Type	pH	Free Acidity	Total Acidity
Red spruce	4.3	50 μeq/L	500 μeq/L
Northern hardwood	5.0	10 μeq/L	500 μeq/L

These leachate solutions are being chemically analyzed for common ions, including nitrate, sulfate, chloride, sodium, potassium, and ammonium, as well as total organic carbon.

At Georgia Tech, Steven Serkiz, a PhD student in Geophysical Sciences, has begun work on this project. Steve has worked on installation of the automatic titration apparatus and on development of computer software for controlling the titration apparatus and for analysis of titration data in terms of the Gaussian distribution model that has been developed by Perdue and coworkers. In the next two months, soil litter sample extractions will be conducted to obtain sufficient quantities of humic substances to determine their acidic properties.

6-35-642

The Contribution of Leachable Organic Acids in Forest Soils
to the Acidification of Surface Waters

Letter Report No. 2 - Submitted on Februar 17, .986

by E. M. Perdue and R. W. Garber

Research has continued at the TVA laboratory on Task II, specifically that part of this Task that addresses the effect of temperature on the yield of soluble organic acids from soil litter samples. The experimental procedure has been modified to simultaneously examine the effect of litter leaching frequency on organic acid yields. Twenty-four leaching columns were filled with 20 grams (a two-inch depth) of litter from beneath red spruce and mixed hardwoods in the Raven Fork watershed and leached for eight hours with 200 mL of deionized water to "initialize" the samples by removing any water-soluble components. The last 20 mL of leachate solution was used to define an initial state (0-Day Sample) for each sample. One half of the leaching columns were subdivided into four groups of three replicates each (they will be called 2-day, 4-day, 8-day, and 16-day samples, respectively) and stored at 15°C. The other half of the leaching columns were similarly subdivided and stored at 3°C. The 2-day, 4-day, 8-day, and 16-day samples were leached with deionized water every 2, 4, 8, or 16 days for a total of 16 days. Each leachate solution was analyzed for pH, total acidity, NO_3^-, SO_4^{2-}, NH_4^+, K^+, and Na^+. Calcium and magnesium ions were below detection limits of ion chromatography.

The data from these leaching experiments are not yet fully analyzed. Some trends have been observed with respect to the effects of both leaching frequency and storage temperature on the yield of soluble acids from soil litter samples. A partial table of initial results for pH and Total Acidity (T. A.) is given below.

Sample	Red Spruce Litter pH	T. A. (µeq/L)	Hardwoods Litter pH	T. A. (µeq/L)
0-Day	5.6	140	5.5	90
2-Day (3°C)	5.6	310	5.2	230
16-Day (3°C)	4.0	530	4.9	240
2-Day (15°C)	5.1	530	4.9	240
16-Day (15°C)	3.9	1000	4.9	280

In addition, both NO_3^- and NH_4^+ tend to increase with temperature and storage time between leachings, the effect being most pronounced in red spruce litter samples. The total yield of ionized acids from red spruce litter samples is greater if the samples are leached eight times at 2-day intervals than for a single leaching after 16 days of storage, possibly due to dilution effects on the degree of ionization of organic acids.

Future experiments will examine the effects of leaching rate, moisture content of litter, and pH of leaching solution on the yield of titratable acids from the two types of forest litter samples. In addition, large-scale leaching experiments will be conducted to provide the Georgia Tech lab with 1200 mL of leachate solution for each treatment. Those solutions can then be used for Task III. Task IV will be carried out in late spring, when the streams should contain relatively high levels of dissolved organic carbon.

At Georgia Tech, the instrumentation and software for conducting and analyzing titrations of litter leachate organic acids are essentially ready. We will begin those studies in the last half of March, when Dr. Garber can conduct large-scale leaching experiments to produce the 1200 mL solutions from which soil organic acids will be isolated. In the meantime, we have begun a long-term effort to streamline the extraction procedures that we ordinarily use to isolate soil organic acids. Our experience on another project at the Coweeta Hydrologic Laboratory clearly indicates that we are severely time-limited by the current methods. Preliminary results indicate that column leaching with alkaline solutions compares with alkaline batch extractions and produces a much more concentrated solution for subsequent cleanup. We are attempting to optimize the column extraction method for future studies that require extractions of soil organic acids (such as the proposal we are currently submitting to John Huckabee at EPRI).

G-35-642

The Contribution of Leachable Organic Acids in Forest Soils

to the Acidification of Surface Waters

Letter Report No. 3 - Submitted on May 26, 1986

by E. M. Perdue and R. W. Garber

This Letter Report summarizes the current project status and modifications to the original work plan that were verbally accepted by John Jansen.

Current Status

A preliminary leaching study of the soil litter samples from a red spruce forest and a northern hardwoods forest has been completed. Soil litter samples were repetitively leached with deionized water as described in the previous Report. The time studies of weak acid production have yielded the data that are appended to this Report. It is evident that nitrification is a major biochemical process in the leaching columns, and that this process is enhanced by frequent leaching, which temporarily raises litter pH values to a more favorable level for the nitrification process. The litter samples are also losing potassium to solution at a high rate. Much, but not all, of the weak acidity in the leachate solutions is ammonium ion. The remaining weak acidity is presumably organic acids.

We have received the first batch leachate solution at Georgia Tech and have just begun our ultrafiltration cleanup procedure to desalt the sample. After inorganic cations and anions have been reduced in concentration by continuous ultrafiltration with dilute HCl, the samples will be freeze-dried to isolate leachate organic acids. At that time, elemental and functional group analyses and acid-base titrations can be conducted.

On May 12th, we collected 220 L of Raven Fork stream water at the Cherokee Trout Farm. We had hoped to wait for a heavy rain before sampling, but finally gave up and sampled under drought conditions. The sample has already been concentrated to 20 L using the large-scale reverse osmosis concentration unit and is being prepared for ultrafiltration cleanup at this time.

The project is running somewhat behind schedule, necessitating a postponement of the completion date to November 1, 1986, by which time we expect to be able to provide Southern Company Services with a draft final report. In the meantime, if no major obstacles hinder our efforts to desalt the batch leachate solutions, we should be able to submit a draft outline of our final report by August 15th.

Modifications to Work Plan

The original work plan called for each soil litter sample to be subjected to a series of leaching tests that were designed to evaluate the effects of (1) rain rate, (2) rain acidity, (3) litter moisture between leachings, and (4) temperature on the production of weak acids. The conditions used are summarized in the following table with the "standard" conditions underlined.

Experimental Parameter	Range of conditions					
rain rate	0.25	0.5	<u>1.0</u>	2.0	4.0	cm/hr for 5 cm (22 mL)
rain acidity	pH 4.0	<u>pH 5.7</u>				adjusted with 2:1 H_2SO_4:HNO_3
litter moisture	<u>moist</u>	dried				leached 4 times at weekly intervals
temperature	3°C	<u>15°C</u>				leached 4 times at weekly intervals

The original matrix requires a minumum of 18 leaching experiments per sample, each experiment run in triplicate. In the original proposal, we planned to match each analytical scale leaching experiment with a batch scale experiment to obtain sufficient organic acids for detailed elemental and functional group characterization. The time required to accomplish that task is simply too great. Furthermore, because every leachate solution in the analytical experiments is titrated to determine total titratable acidity, we have sufficient information from the analytical experiments to detect any major differences in the chemical properties of the weak acids in any two leachate solutions. We have therefore proposed that the number of batch leaching experiments be reduced to nine per sample. For each Experimental Parameter in the preceding table, we will prepare the following number of batch leachate solutions per litter sample: rain rate (1), rain acidity (1), litter moisture (3), temperature (4). If the analytical titration experiments reveal unusual variations in the chemical properties of weak acids, additional batch leachate solutions will be prepared.

In the litter moisture and temperature experiments, we have elected to do a much more comprehensive series of leaching experiments than originally proposed. Rather than leaching each sample at weekly intervals for four weeks, we will use the experimental protocol used to generate the appended data. Each sample will be "initialized" by exhaustive leaching with deionized water. Four separate columns of soil litter (2-day, 4-day, 8-day, 16-day) will be prepared and leached at 2, 4, 8, and 16 day intervals for a total of 16 days. We believe that this protocol is more suited to detection of temporal trends and simultaneously examines the effect of an additional parameter, rain frequency, on the mobilization of organic acids from forest soil litter.

Litter Leaching Studies - Southern Co. Project - TVA
20 g. moist soil in column packed to a density of 1 g/mL
Leached with water (1 cm/hr for 5 hr) - about 22 mL

Sample: Red spruce forest soil litter at 15°C

	Day	pH	[H+]	[K+]	[NH4+]	Organic Acid	[NO3-]
2-Day	2	5.13	9	107	325	198	37
	4	4.95	13	114	267	65	42
	6	5.10	9	118	201	65	52
	8	4.83	17	110	161	70	75
	10	4.80	19	104	141	60	81
	12	4.86	16	126	100	86	100
	14	4.44	43	141	101	78	100
	16	4.27	63	136	76	28	111
4-Day	4	4.62	28	145	400	180	44
	8	4.54	34	128	311	117	54
	12	4.45	42	113	267	51	91
	16	4.16	81	121	214	11	100
8-Day	8	4.47	40	161	440	202	63
	16	4.24	68	142	416	29	104
16-Day	16	3.95	132	193	549	286	116

Sample: Red spruce forest soil litter at 3°C

	Day	pH	[H+]	[K+]	[NH4+]	Organic Acid	[NO3-]
2-Day	2	5.60	3	65	195	104	7
	4	5.54	3	55	177	41	4
	6	5.82	2	53	167	-11	3
	8	5.59	3	47	148	1	4
	10	5.74	2	48	142	-2	5
	12	5.66	3	36	134	-21	2
	14	5.48	4	29	118	10	5
	16	5.31	6	39	110	-13	9
4-Day	4	5.18	8	81	221	106	9
	8	5.33	6	57	150	76	9
	12	5.37	5	41	132	65	8
	16	5.34	5	31	121	57	9
8-Day	8	4.94	14	91	256	162	12
	16	5.04	11	77	196	136	9
16-Day	16	4.88	16	108	328	233	19

Sample: Northern hardwood forest soil litter at 15°C

	Day	pH	[H+]	[K+]	[NH4+]	Organic Acid	[NO3-]
2-Day	2	4.89	15	141	121	106	41
	4	4.98	12	150	108	113	52
	6	4.92	14	140	101	165	67
	8	5.10	9	112	87	134	51
	10	5.06	10	100	90	60	71
	12	5.24	7	104	101	29	67
	14	5.06	10	94	81	59	80
	16	5.18	8	118	76	9	81
4-Day	4	4.88	16	150	163	104	57
	8	4.97	13	121	141	126	71
	12	5.15	8	104	111	74	77
	16	5.04	11	97	97	35	57
8-Day	8	4.90	15	167	179	139	73
	16	4.92	14	121	121	85	77
16-Day	16	4.91	14	181	198	71	88

Sample: Northern hardwood forest soil litter at 3°C

	Day	pH	[H+]	[K+]	[NH4+]	Organic Acid	[NO3-]
2-Day	2	5.14	9	85	111	116	30
	4	5.11	9	88	100	47	37
	6	5.07	10	70	97	93	40
	8	5.18	8	71	81	71	33
	10	5.26	6	65	85	38	30
	12	5.26	6	60	67	20	35
	14	5.30	6	60	60	47	27
	16	5.35	5	71	55	27	24
4-Day	4	5.09	10	92	121	82	38
	8	5.05	10	82	107	105	44
	12	5.06	10	76	100	63	35
	16	5.21	7	59	80	56	30
8-Day	8	4.96	13	97	142	112	47
	16	5.02	11	81	111	91	40
16-Day	16	4.94	14	103	161	75	59

G-35-642

DRAFT

THE CONTRIBUTION OF LEACHABLE ORGANIC ACIDS IN FOREST SOILS TO THE ACIDIFICATION OF SURFACE WATERS

Outline of Final Report - Submitted on February 6, 1987

by

E. M. Perdue and S. M. Serkiz

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and

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Muscle Shoals, AL 35660

to

Southern Company Services, Inc.

P.O. Box 2625

Birmingham, AL 35202

Attention: John J. Jansen

I. Overview

A. This study has investigated some of the factors that are thought to affect the mobilization of organic material and inorganic cations/anions from forest soil litter. The factors considered are:

1. forest litter type
2. temperature
3. moisture content of litter
4. pH of leaching solution
5. frequency of leaching events
6. intensity of leaching events.

Unique components of the study are the examination of the effects of the above factors on the chemical characteristics of mobilized organic acids (elemental and acidic functional group analyses) and analysis of titration data to determine the acidic strengths (pK_a's) of the organic acids.

B. The natural and anthropogenic fluxes of acidity through forested watersheds into surface waters are compared, and the Gran titration method for estimation of strong and weak acidity in surface waters is evaluated in light of data obtained in (A).

II. Experimental

A. Analytical scale leaching studies at the TVA are designed to determine the effects of the parameters in (I) on the mobilization of strong and weak acidity from forest soil litter.

1. forest litter type
   a. Red spruce litter
   b. Northern hardwoods litter

2. temperature
   a. 24°C
   b. 3°C

3. moisture content of litter
   a. Moist - samples used as is, not dried between successive leaching experiments.
   b. Dry - samples air-dried for eight hours after each leaching experiment.

4. pH of leaching solution
   a. pH 5.7
   b. pH 4.0
   c. pH 3.5

NOTE: The pH 5.7 leaching solution has the following composition in μeq/L: $[H^+] = 2$, $[Na^+] = 5$, $[K^+] = 2$, $[NH_4^+] = 12$, $[Mg^{2+}] = 5$, $[Ca^{2+}] = 11$, $[HCO_3^-] = 2$, $[Cl^-] = 12$, $[NO_3^-] = 12$, $[SO_4{}2^{2-}] = 11$. A 2:1 (equivalent ratio) mixture of $H_2SO_4:HNO_3$ was added to this solution to produce pH 4.0 and 3.5 solutions.

5. frequency of leaching events
   a. 2-day intervals
   b. 4-day intervals
   c. 8-day intervals
   d. 16-day intervals

6. intensity of leaching events.
   a. 0.25 cm/hr
   b. 0.50 cm/hr
   c. 1.00 cm/hr
   d. 2.00 cm/hr
   e. 4.00 cm/hr

B. Large scale leaching samples prepared by TVA for characterization of leachable organic acids by Georgia Tech.

1. Sample preparation at TVA

2. Isolation and purification of organic acids
   a. Inorganic anions and some cations removed by ultrafiltration
   b. Remaining cations removed by cation exchange resin
   c. Vacuum evaporation and lyophilization to obtain dried products

3. Elemental and functional group analyses
   a. organic and inorganic carbon balances on leachate solutions, isolated organic matter, and soil samples.
   b. carbon, nitrogen, hydrogen content of isolated organic matter.
   c. acid-base titrations of isolated organic matter.
   d. data fitting, via the gaussian distribution model, to give concentrations and acidic strengths (pKa's) of organic acids.

C. Isolation and characterization of organic acids from Raven Fork Creek

1. Collection of water samples

2. Isolation and purification of organic acids
   a. Initial desalting on cation exchange resins
   b. Reverse osmosis to produce highly concentrated solution
   c. Ultrafiltration and desalting for further purification
   d. Lyophilization to obtain dried product.

3. Elemental and functional group analyses
   a. carbon, nitrogen, hydrogen content of isolated organic matter.
   b. acid-base titrations of isolated organic matter.
   c. data fitting, via the gaussian distribution model, to give concentrations and acidic strengths (pKa's) of organic acids.

D. Examination of errors in the Gran titration method.

1. Average acidic functional group concentrations and acidic strengths are used to generate alkalinity and acidity titration data for various compositions of DOC, DIC, and strong inorganic acidity.

2. The generated titration data sets are analyzed for strong and weak alkalinity and acidity endpoints using the Gran method of analysis of titration data.

III. Results

A. Analytical scale leaching experiments

1. forest litter type - preliminary results indicate greater mobilization of organic acids from red spruce litter than from the northern hardwoods litter under otherwise similar leaching conditions.

2. temperature - preliminary results indicate that the yields of leachable organic acids increase with increasing temperature.

3. moisture content of litter - preliminary results indicate a greater rate of production of leachable organic acids in dried litter, probably due in part to a more complete re-oxygenation of the sample during the drying process.

4. pH of leaching solution - preliminary results indicate a very small tendency for greater yields of leachable organic acids at higher pH values. The pH values of leachate solutions, however, are virtually identical in all cases, even though the initial leaching solutions ranged from pH 5.7 to pH 3.5.

5. frequency of leaching events - preliminary results indicate that the actual concentration of leachable organic acids obtained in a single leaching event is lower in frequently leached samples; however, greater cumulative yields of leachable organic acids are obtained by frequent leachings.

6. intensity of leaching events - preliminary results indicate that total acidities are greater at lower leaching rates but little effect is found on common inorganic ions.

B. Large scale leaching studies for organic matter characterization.

1. Recoveries, losses, and final yields of leachable organic acids
2. Elemental analyses
3. Acid-Base titrations
4. Gaussian distribution modeling results

C. Isolation and characterization of organic acids from Raven Fork Creek

1. Yields of stream organic acids
2. Elemental analyses
3. Acid-Base titrations
4. Gaussian distribution modeling results

D. Examination of errors in the Gran titration method.

1. General discussion of Gran method

2. Presentation of generated data sets at variable DOC, DIC, and strong inorganic acidity.

3. Results of Gran analyses for strong and weak alkalinity and acidity endpoints - preliminary results indicate that about 52% of the carboxylic acid functional groups in forest litter leachates will appear as <u>strong</u> acids in a Gran analysis of acidity titration data and that up to 48% of the carboxyl groups will be included in Gran estimates of the alkalinities of such solutions.

IV. Discussion

A. Factors that influence the rates of production of leachable organic acids in forest litter.

B. Some predictions of relative contributions of internally generated organic and inorganic acids and atmospherically derived inorganic acids to watershed acidification.

C. Comparison of this study with other soil leaching studies, particularly those conducted by TVA personnel.

D. Discussion of the limitations of the Gran method in distinguishing between "strong" and "weak" acidity in surface waters

V. Summary

VI. References

THE CONTRIBUTION OF LEACHABLE ORGANIC ACIDS IN FOREST SOILS TO THE ACIDIFICATION OF SURFACE WATERS

Final Report - Submitted on January 8, 1989

by

E. Michael Perdue and Steven M. Serkiz
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to

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EXECUTIVE SUMMARY

Soil organic acids are abundant, quite acidic, and relatively mobile in forested ecosystems. Accordingly, they are a potentially significant source of acidity in those environments, and their importance relative to acidic deposition is not well documented. This study tests the hypothesis that the concentrations and acidic properties of soil organic acids are functions of environmental conditions in soil litter between and during storm events.

Forest litter samples were collected from the Raven Fork watershed in the Great Smoky Mountains National Park. Litter samples from red spruce and northern hardwoods ecosystems were leached under a variety of controlled laboratory conditions to examine the effects of the following parameters on concentrations and acidic properties of litter-derived organic acids: (1) pH of leaching solution, (2) litter storage temperature, (3) litter moisture content, (4) leaching intensity, (5) leaching frequency, and (6) litter type. Furthermore, dissolved organic matter from Raven Fork Creek was isolated, characterized, and compared with the litter-derived organic acids.

The average carboxylic acid content (COOH) of litter-derived organic acids was 5.0 ± 1.5 milliequivalents per gram of organic carbon. No systematic effects of sample storage or leaching conditions on COOH values were observed. The actual amount of dissolved organic carbon (DOC) that was mobilized from litter samples, however, was dependent on experimental conditions. Long periods of storage between leaching events, higher temperatures, and drier conditions all tended to increase the DOC concentrations of leachate solutions. Interestingly, the nature of the leaching event itself (pH of leaching solution, leaching rate, etc.) had little effect on the mobilization of DOC and organic acidity. Red spruce litter generally yielded more leachable organic acids than northern hardwoods litter.

The elemental compositions and acidic properties of litter-derived organic acids were insensitive to sample storage and leaching conditions. All samples could be succinctly described as a broad distribution of acidic functional groups with a mean pK_a (μ) of 4.9

and a standard deviation (σ) of 1.6 pK_a units. The Raven Fork Creek sample, on the other hand, had μ and σ values of 3.0 and 1.8, respectively.

Because sample storage and leaching conditions do not affect either the acidic content or acidic strengths of litter-derived organic acids, average intrinsic properties of these acids can be used in models of watershed acidification, i.e. organic acid concentrations in litter leachate solutions are directly proportional to DOC concentrations. The flux of organic acidity (milliequivalents per square meter) that can be generated by *R* meters of rain passing through a forest litter horizon during a storm event is:

$$\text{Organic Acidity (meq/m}^2) = \text{DOC} * \text{COOH} * \text{R} * (1 \text{ meq-l}/\mu\text{eq-m}^3),$$

where DOC, COOH, and *R* are in units of milligrams of organic carbon per liter (mg C/l), microequivalents per milligram of organic carbon (μeq/mg C), and meters (m). Under the conditions of this study, the estimated annual flux of organic acidity from soil litter horizons is more than 31 times the annual flux of acidity in rainfall in the Raven Fork watershed (1 meter of rain with an average pH of 4.9).

To predict actual fluxes of organic acidity (or DOC) from forest litter during storm events, it will be necessary to consider antecedent conditions such as temperature and moisture content of litter and the elapsed time between storm events. The amount of organic acidity that eventually reaches a stream depends on the flux of litter-derived organic acids and on processes that remove and/or transform those acids during their passage through the soil environment. Even though only about three percent of initially mobilized organic acidity in the Raven Fork watershed eventually reaches Raven Fork Creek, the annual flux of organic acidity roughly equals the annual atmospheric flux of acidity. The acidic strength of organic matter in the stream is much greater than that of the litter-derived organic acids.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF ILLUSTRATIONS

OVERVIEW

The abundances, acidic strengths, and mobilities of soil organic acids are sufficiently great that they should be regarded as a potentially major contributor to the natural background acidification of forest soils and surface waters. Despite the fact that the chemical characteristics of these acids are extensively documented in the organic geochemical literature, their contribution to watershed acidification is often overlooked or dismissed in quantitative assessments of the effects of "acid rain" on forested ecosystems. This report will demonstrate that organic acids in forest litter in the Raven Fork watershed, located in the Great Smoky Mountains National Park, are:

(1) present in the upper layers of forest soils at instantaneous levels that far exceed a year's input of highly acidic "acid rain",

(2) readily leached from soil litter into surface waters at such concentrations that the annual export of organic acidity from forest soils in the Raven Fork watershed is approximately equal to a year's input of highly acidic "acid rain" to those soils,

(3) continually replenished by decomposition of biomass on the forest floor,

(4) much less acidic than the organic acids that eventually reach Raven Fork Creek. The stronger soil-derived organic acids that reach surface waters are easily capable of producing the low pH values that are often observed in brown-colored surface waters and in clear, but poorly buffered, surface waters.

To better understand the processes of formation, mobilization, and transport of organic acids in forest soils, several factors that reportedly affect these processes have been examined. Given our initial view that the formation of organic acids is biologically mediated and that their mobilization and transport are affected both by chemical and hydrological factors, the following factors were included in the study.

(1) Forest litter type. The rate and extent of conversion of biomass into soil organic acids by soil microorganisms could vary with the nature of the biomass. Soil litter

samples were collected from two areas of the Raven Fork watershed, one of which contains predominantly red spruce (RS) and the other of which contains mixed northern hardwoods (NH).

(2) Temperature. Microbial production of soil organic acids should vary seasonally with temperature, being higher in summer than in winter. Two temperatures (3 °C and 24 °C) were used to simulate the effects of seasonal temperature changes on organic acid production in this study.

(3) Moisture content of litter. High moisture content may inhibit diffusion of oxygen into the litter, thereby favoring anaerobic degradation pathways. Biologically mediated oxidation of biomass thus may vary both quantitatively and qualitatively with the moisture content (redox conditions) in forest soil litter. Organic acid production was thus studied in both moist and dry litter samples.

(4) pH of leaching solution. Because the solubilities of organic acids and metal-organic salts are functions of pH, the mobilization and transport of soil organic acids is expected to be a function of the pH of the leaching solution. Synthetic rainfall solutions of pH 5.6, 4.0 and 3.5 were used to examine this factor.

(5) Frequency of leaching events. The accumulation of organic acids and other products of microbial decomposition of biomass during the intervals between precipitation events may affect the rate and extent of microbial degradation through a variety of feedback mechanisms (e.g., suppression of the nitrification process at low pH, nutrient transport, and waste removal). This factor was examined by leaching soil litter at 2, 4, 8, and 16-day intervals.

(6) Intensity of leaching events. The kinetics of mobilization of soluble organic acids depends on both the inherent rates of the chemical dissolution processes and the length of contact time between leaching solution and soil litter. The effect of rainfall intensity (and thus contact time) on mobilization of organic acids was examined using simulated rainfall rates of 0.25, 0.5, 1.0, 2.0, and 4.0 cm/hr.

In conjunction with the investigation of the processes of formation, mobilization, and transport of organic acids in forest litter, the mobilized organic acids have been chemically characterized. The effects of the above six factors on the chemical properties of the mobilized organic acids were assessed through measurements of elemental composition and concentrations of major acidic functional groups. Differences in chemical properties of organic acids that were mobilized under dissimilar leaching conditions indicate either (1) different source materials, (2) preferential extraction of some components of the litter under varying conditions, or (3) differences in the microbiological processes that produce mobilizable organic acids.

To further characterize the mobilized organic acids and, specifically, to make it possible to predict their effects on pH and acid neutralizing capacity of poorly buffered waters, the acidic strengths of the major classes of acidic functional groups were determined. Alkaline titration data were analyzed with the Gaussian distribution model of Perdue and coworkers to obtain realistic estimates of the spectrum of pK_a's in these highly complex mixtures.

This study focuses mainly on formation and mobilization of organic acids in forest litter from the Raven Fork watershed; however, not all of the mobilized organic acids are expected to ultimately reach surface waters. The chemical properties of dissolved organic matter (DOM) in local surface waters are thus likely to differ from those of litter-derived organic acids. To examine this possibility, a DOM sample was collected from Raven Fork Creek and subjected to the same analyses as the litter-derived samples.

Given a viable mathematical description of the acid-base properties of mobilized organic acids and measurements of their acidic functional group concentrations, a series of computer simulations of acidity and alkalinity titrations were generated. These "data" were used to evaluate the Gran method, which is widely used to separately quantify strong and weak acids in a water sample. This evaluation provides insight into the effects of organic acids on acidity and alkalinity measurements.

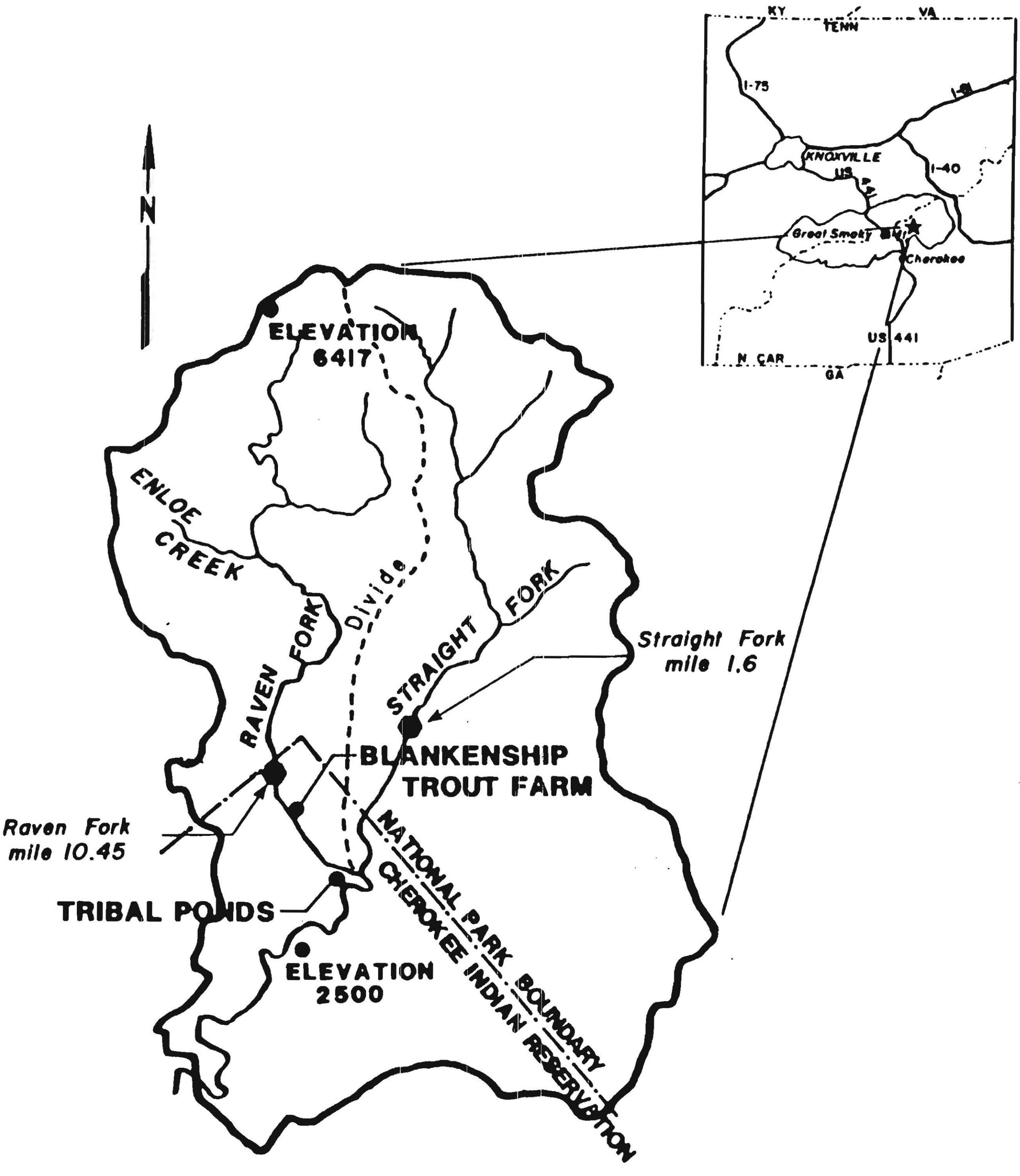
EXPERIMENTAL

Litter Collection

Samples of forest litter were collected from two sites in the Raven Fork watershed, which is a remote, high-elevation watershed in the Great Smoky Mountains National Park (Fig. 1). This watershed was chosen because of its remoteness (minimal anthropogenic influence) and because it has been a subject of some previous studies by TVA. One sample collection site had a principal cover of red spruce (RS) while the other had a mixed northern hardwoods (NH) cover.

Sample collection was carried out early in June, 1985, as soon as access to the collection sites could be assured (winter weather conditions can prevent access to these sites until late spring). A quantity of litter that was sufficient for the entire study (several kilograms) was collected from each site. The material collected was the upper 1-3 cm of soil litter and was composed principally of identifiable leaf or needle fragments, probably from the previous fall. Litter collection was carried out manually to avoid contamination of the recent litter with highly decomposed leaf litter that was present immediately below the recent litter. Soil temperature at the time of collection was between 8 °C and 10 °C.

Litter samples were placed in new polyethylene bags, which were placed in burlap bags for transport out of the watershed. After transport from the remote watershed, which required about six hours, the samples were placed in Styrofoam coolers with ice for transport to the laboratory. At the laboratory, all litter material was stored in refrigerators maintained at 3 °C. The forest leaf litter samples were quite heterogeneous in structure, color, etc., so, prior to the leaching experiments, the leaf litter material from each site was manually mixed to decrease sample heterogeneity.



RAVEN FORK AND STRAIGHT FORK WATERSHEDS

Figure 1 . Raven Fork and Straight Fork Watersheds.

Collection of Surface Water Sample

A fifty-five gallon sample of water from Raven Fork Creek was collected in 20-liter polyethylene carboys in May, 1986. The water sample was taken at a site just above the water intake to Blankenship's Trout Farm, where Raven Fork Creek exits the Smoky Mountain National Park (see Figure 1). At the time of sample collection, this area was experiencing a period of extended drought and water levels in the creek were quite low. Water samples were transported to Georgia Tech, stored at 4 °C, and processed within three days.

Litter Leaching Experiments

A series of leaching experiments was designed to separately examine the effects of the six factors that were described in the previous section on the processes of formation, mobilization, and transport of organic acids in forest soils:

(1) forest litter type

(2) litter temperature

(3) moisture content of litter

(4) pH of leaching solution

(5) frequency of leaching events

(6) intensity ("rain" rate) of leaching events.

The arbitrarily selected standard conditions for these leaching experiments for a given type of litter are: moist litter samples stored at room temperature (24 °C) and leached every two days with pH 5.6 synthetic rain at a "rain" rate of one cm/hr for five hours.

Synthetic rain was prepared from deionized water (resistance 16.7 MΩ-cm or higher) to which Na^+, K^+, Mg^{2+}, Ca^{2+}, NH_4^+, Cl^-, NO_3^-, and SO_4^{2-} were added at concentrations of 5, 2, 5, 11, 12, 12, 12, and 11 μeq/L, respectively. These concentrations were suggested by Lee and Weber (1980) and were based on a 7-year average for precipitation collected at Hubbard Brook, New Hampshire (Likens and Bormann, 1975), after correction for estimated sulfuric and nitric acid components. The resultant solution was equilibrated with atmospheric CO_2 to obtain a synthetic rain with a pH between 5.5 and 5.8 (subsequently designated as pH 5.6 synthetic rain). Acidic rain (either pH 4.0 or 3.5) was prepared by amending the pH 5.6 synthetic rain with sulfuric and nitric acid (2 to 1 on an equivalent basis, respectively). Synthetic rain solutions were freshly prepared every 10 days to minimize microbial contamination.

Litter samples were leached using a chemical vacuum extractor designed and manufactured by Concept Engineering, Inc., Lincoln, Nebraska. This device utilizes 60 ml plastic syringes in a tandem arrangement to hold the leaching fluid, the litter and the final leachate (Fig. 2). This arrangement minimizes gas exchange between the leachate solution and the laboratory atmosphere. The electrically powered apparatus can be controlled to generate a wide range of leaching rates (0.1 to 24 cm of "rain" per hour).

In a typical leaching experiment, 20 g of forest litter was weighed and placed into leaching tubes and packed to a litter depth of approximately 5 cm, which is slightly greater than the thickness of the litter at the sample sites. A 5-cm depth of synthetic rain (approximately 38 ml) was placed in each reservoir tube in the extractor apparatus. The synthetic rain was applied at the rate specified for the experiment and the leachate solution was collected. At the conclusion of the leaching experiment, the leachate solution was removed from the leachate syringe, placed into a clean polypropylene test tube, sealed and refrigerated until analysis. A sufficient number of these leaching columns was utilized (in parallel) to provide about 1200 ml of litter leachate solution in each experiment.

Preliminary leaching experiments indicated that leachate samples were quite variable in composition, due in part to the sample heterogeneity but also caused by variations in sample packing in the leaching apparatus. It is estimated that ten or more replicates of each leaching experiment would be needed to statistically overcome these problems. Because there were inadequate resources at TVA for this level of replication, each experiment was replicated only three times.

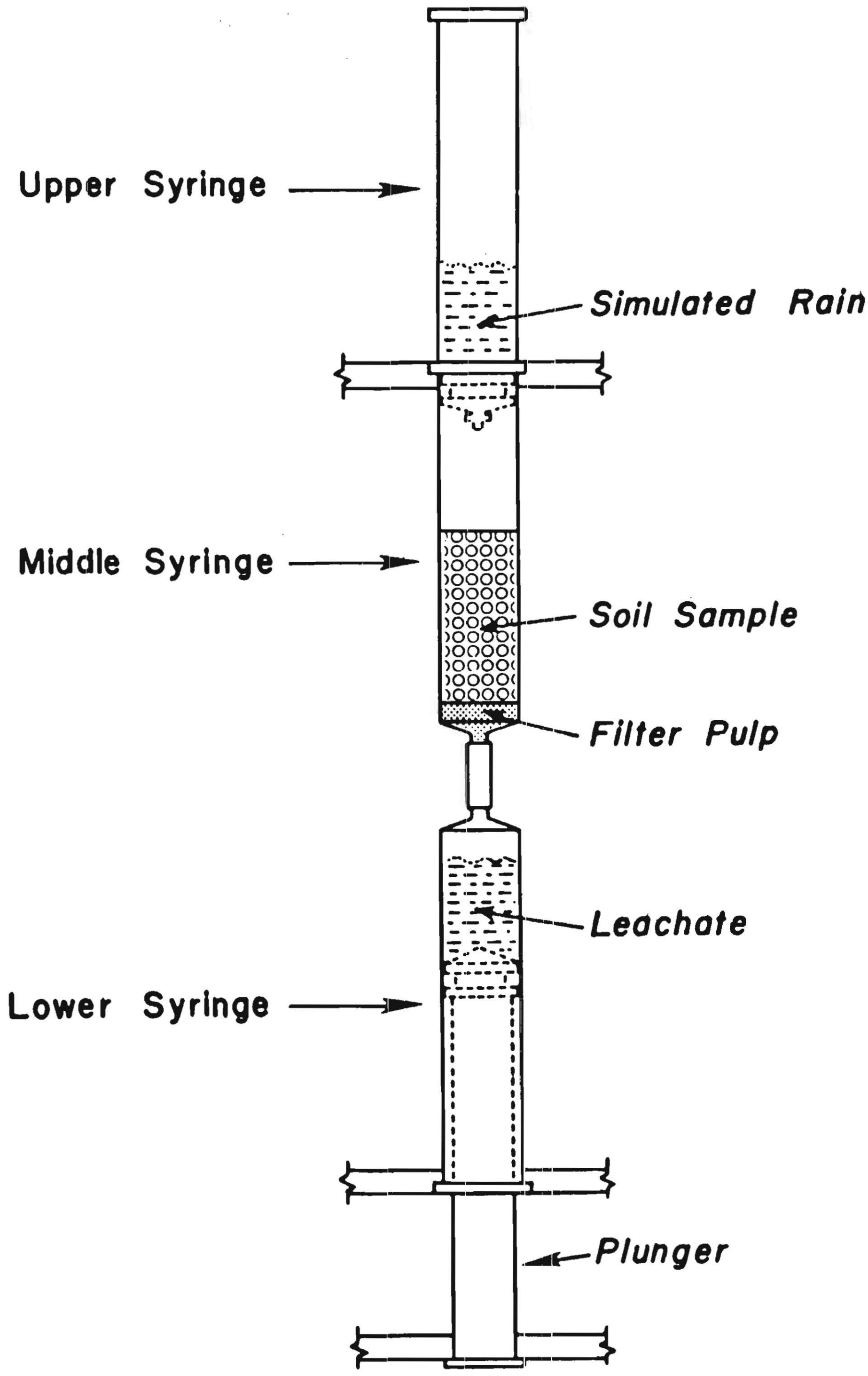


Figure 2. Schematic of Leaching Apparatus.

Forest Litter Type

The rate and extent of conversion of biomass into soil organic acids by soil microorganisms could vary with the nature of the biomass. Previous TVA studies in the Raven Fork watershed indicated that there were qualitative and quantitative differences in leachable organic acids from forest litters of different vegetation type (Jones et al., 1983; Noggle et al., 1984). This factor was evaluated by conducting all leaching experiments on two quite different litter samples, one from a predominantly red spruce forest (RS) and the other from a predominantly mixed northern hardwoods forest (NH).

Litter Temperature

Microbial production of soil organic acids should vary seasonally with temperature, being higher in summer than in winter. The effect of temperature on the long-term release of organic acids from forest litter was studied by comparing leachate solutions obtained under standard conditions with those obtained at 3 °C. Specifically, litter samples were stored between successive leachings at either 24 °C or 3 °C for a total of 32 days. This set of experiments was also used to evaluate leaching frequency effects (see subsequent discussion).

Moisture Content of Litter

High moisture content may inhibit diffusion of oxygen into the litter, thereby favoring anaerobic degradation pathways. Biologically mediated oxidation of biomass thus may vary both quantitatively and qualitatively with the moisture content (redox conditions) in forest soil litter. Organic acid production was studied by comparing leachate solutions obtained under standard conditions (moist) and dry conditions. Specifically, litter samples were stored between successive leachings over a ten-day period either in a moist condition (excess water was displaced from the litter column with air) or in a dry condition (litter samples were allowed to completely air-dry).

pH of Leaching Solution

Because the solubilities of organic acids and metal-organic salts are functions of pH, the mobilization and transport of soil organic acids is expected to be a function of the pH of the leaching solution. The effect of synthetic rain pH on litter leachate composition was studied by successively leaching litter samples over a ten-day period, using either standard leaching solution (pH 5.6) or acidified synthetic rain (pH 4.0 or 3.5). All other leaching parameters were maintained at standard conditions.

Frequency of Leaching Events

During the intervals between precipitation events, organic acids and other products of microbial decomposition of biomass accumulate in forest litter, possibly affecting, in turn, the rate and extent of the microbial degradation processes. These substances are rapidly mobilized from forest litter during a precipitation event, and can cause large temporal variations in the concentrations of soil-derived organic acids in streams. The magnitude of these effects should depend on both the amount of accumulated organic acids in the litter and the intensity of the event. The effect of leaching frequency was evaluated by leaching litter samples at 2, 4, 8, and 16-day intervals over a 32-day period. These experiments were also used to evaluate temperature effects (see previous discussion).

Intensity of Leaching Events

The effect of rainfall intensity (and thus contact time between leaching solution and soil litter) on the extent of mobilization of organic acids depends on the relative rates of many chemical and transport processes. This factor was examined by successively leaching litter samples with synthetic rain at the standard rate (1.0 cm/hr) and at rates of 0.25, 0.5, 2.0, and 4.0 cm/hr for a six-day period. All other leaching parameters were maintained at standard conditions.

Analysis of Litter Leachate Solutions

The chemical characterization of each leachate included concentrations of selected inorganic cations and anions, pH, total and weak acidity, and total organic carbon. All reagents, buffers, and other chemicals were reagent-grade commercial products. More specific information is provided below.

Major Cations and Anions

Principal cations (K^+, NH_4^+) were measured using a Dionex QIC ion chromatograph equipped with a Dionex CS1 analytical column. The eluent used was 5mM HCL. A Dionex micromembrane cation suppressor was used with a 40 mM tetramethylammonium hydroxide regenerant. The limits of detection were 5 μeq/L for K^+ and 3 μeq/L for NH_4^+. Major anions were determined using a Biorad model 300 liquid chromatograph which was equipped with a Dionex AS4A analytical column and a Dionex AG4A guard column. Elution was carried out with a solution containing 1.7 mM $NaHCO_3$ and 2.3 mM Na_2CO_3. Suppression was accomplished with a Dionex micromembrane suppressor using 25 mM sulfuric acid as regenerant. Ion chromatography data were collected, processed and analyzed using an Apple IIe microcomputer equipped with Interactive Microware Chromatochart software and associated data acquisition hardware.

pH, Total Acidity, and Weak Acidity Determinations

Several overall acid-base properties of each litter leachate solution were determined by monitoring solution pH values before and during titration of the solution. A coulometric titration procedure similar to that described by Liberti et al. (1972) was used. A 20 ml aliquot of litter leachate solution was amended with 200 μL of 4M potassium bromide to adjust the ionic strength to 0.04M. This procedure facilitates computation of the concentration of free acidity (H^+) from the initial pH and provides the necessary electrolyte and reactant for the coulometric process. Dissolved carbon dioxide, which would otherwise contribute to the total acidity of a sample, was removed from all solutions by sparging with nitrogen gas prior to and during all titrations. For the titration, hydroxide ions were generated in solution coulometrically using a Princeton Applied Research Corporation (PARC) Model 173 potentiostat/galvanostat equipped with a PARC Model 179 digital coulometer (Fig. 3). The solution pH was monitored continuously with a Radiometer Model PHM 84 pH meter equipped with an Orion semi-micro Ross type combination pH electrode. All titrations were terminated at a final pH of 10.5.

The titration data (pH and amount of OH^- generated) were collected, processed and plotted with an Apple model IIe microcomputer equipped with an Interactive Microware, Inc. ADALAB data acquisition system. The hydrogen ion concentration of the initial leachate solution and each titration point was calculated from the pH, assuming an activity coefficient (0.85) for a solution with the ionic strength established by the concentration of potassium bromide. The data were plotted using the method proposed by Gran (1952) from which the total acidity was obtained. Weak acidity was calculated as the difference between total acidity and the sum of H^+ and NH_4^+ concentrations. A much more complete discussion of this procedure, including its limitations, is discussed in a subsequent section of the report.

Total Organic Carbon

Total organic carbon in each leachate solution was determined using a Coulometrics Model 5030 Total Carbon Analyzer with Coulometer. This instrument oxidizes the organic carbon in a 200 μL aqueous sample by dry combustion in an oxygen stream at 905 °C to CO_2, which is subsequently measured in a coulometric titration cell. The instrument was periodically calibrated against primary standard potassium hydrogen phthalate or sucrose solutions. The detection limit of total organic carbon is 0.2 mg/L.

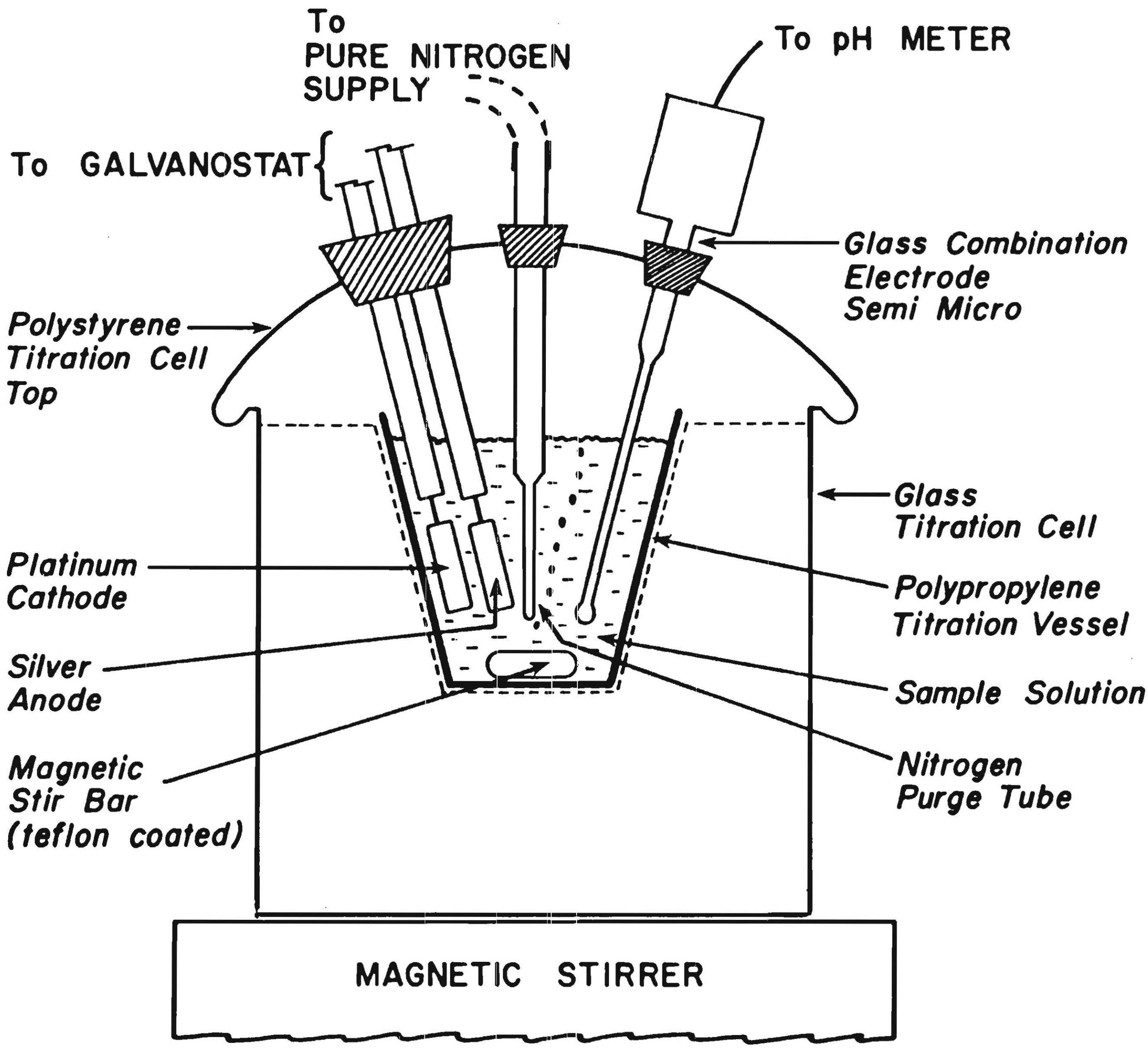


Figure 3. Digital Coulometer.

Isolation and Characterization of Leachate Organic Acids

Isolation and Preparation

One-liter aliquots of selected litter leachate solutions were shipped from TVA to Georgia Tech, where they were processed further to purify and isolate leachate organic acids. The leachate solutions initially contained inorganic and organic particles, 50-250 mg/L of dissolved organic carbon, and a variety of inorganic solutes that were mobilized from the forest litter samples. The Raven Fork Creek water sample, in contrast, contained much lower concentration of DOC ($\approx$ 3 mgC/l) and relatively high concentrations of inorganic solutes.

A reverse osmosis process similar to that reported by Serkiz and Perdue (1990) was used to concentrate 55 gallons of Raven Fork Creek water to a volume of five gallons. The five-gallon concentrated solution was further concentrated to a volume of two liters using a rotating vacuum evaporator at 35 °C. The final concentrated solution was subsequently processed identically to the leaf litter leachate solutions.

The preparation procedure described here was intended to remove the inorganic ions to yield a low-ash freeze-dried organic solid product. As subsequent results will show, however, the effort was only partially successful and many titration results were ultimately unusable. Litter leachate and creek samples were initially centrifuged at 15,000 rpm for 40 minutes to remove particulate matter. After the supernatant solution was decanted, the remaining particulate matter was treated with 0.1N NaOH at pH 9 to recover base-soluble organic matter that had precipitated in the initially acidic leachate solutions. After re-centrifugation, the base-soluble supernatant fraction was added to the original supernatant solution. The base-insoluble particulate matter was removed and dried for use in a final carbon balance.

Major cations, anions, and silica were removed from the DOM solutions by continuous washing with about one liter of 10^{-4} M HCl in a 400-ml stirred ultrafiltration cell that was equipped with an Amicon YM-2 membrane (1000 MW cutoff). The solution containing the organic acids was gradually concentrated to a volume of 200 ml while being freed of soluble inorganic impurities. The solution that passed through the membrane was analyzed for organic carbon, major cations, and sulfate. Organic carbon was analyzed as previously described on a Coulometrics Model 5030 Carbon Analyzer. Standard atomic absorption methods were used to determine the concentrations of major cations (calcium, magnesium, and iron). Sulfate was analyzed by the colorimetric method of Reijnders et. al. 1979. The final concentrated DOM solutions contained less than 0.5 and 0.1 mg/L of major cations and sulfate, respectively.

The ultrafiltration method was unable to completely remove major cations, because those cations form complexes with DOM. The residual major cations were removed by passing the ultrafiltered organic acids through a column of Dowex cation exchange resin (AG50W-X8, H^+-form). The desalted samples were then further concentrated by vacuum evaporation and freeze-dried to obtain an organic acid product. Elemental analyses of carbon, hydrogen, and nitrogen and ash contents were determined on the final isolated solid organic acid samples by a local commercial laboratory.

Organic carbon yields, calculated from the initial TOC values of bulk leachate solutions and the carbon contents of final freeze-dried products, are available for most leachate samples. These data were not, however, available for the creek sample. A complete organic carbon balance at several intermediate points in the isolation procedure was obtained for selected samples.

Functional Group Analysis

Isolated litter leachate organic acids and Raven Creek DOM were titrated with strong base to determine the abundances and acidic strengths of major classes of acidic functional groups. Freeze-dried organic acid samples were redissolved in RO pure water and adjusted to a concentration of 500 mg C/l. A 15-ml aliquot of the 500 mg C/l solution was titrated under $N_2(g)$ at 25 °C with a 0.5 N KOH solution that was standardized against primary standard potassium hydrogen phthalate.

Each entire titration, including electrode calibration and the actual titration, was controlled by a BASIC computer program executing on an IBM XT computer that was equipped with a National Instruments GPIB-PC interface card and a Data Translation DT2805 low level data acquisition board. This system controlled a motor-driven 2.5 ml Gilmont microburet and stirrer system and monitored electrode potentials of a Ross combination electrode that was interfaced to a Hewlett Packard model 3478A multimeter. The Ross electrode was calibrated against commercial pH standards (pH 3.01, 7.39, 9.41) prior to each titration.

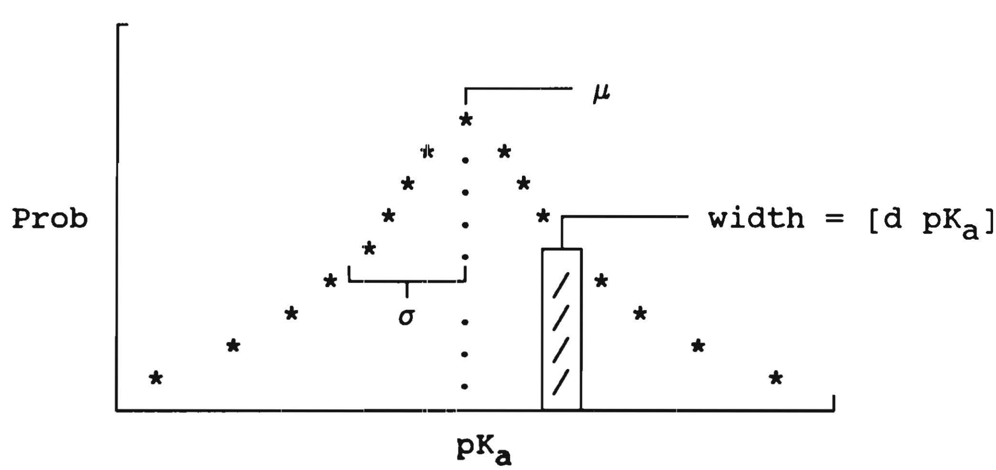
Each pH measurement (standard or sample) was made by monitoring the Ross electrode until either 100 successive voltage reading were within a standard deviation of 0.25 millivolts or a total of 500 voltage readings had been made without the convergence criteria being met. After the electrode calibration procedure was completed, the initial pH of the organic acid solution was determined. Subsequently, increments of titrant were added and stirred to insure adequate mixing with the sample, the stirrer was turned off to establish quiescent conditions in the titration cell, and the pH of the solution was measured. The volume of titrant added in a given increment was automatically adjusted to insure that at least 50 data points would be obtained and to try to cause a pH change of about 0.2 pH units. The total titrant volume used in a titration was the volume needed to reach a final pH of 10.5-11.0, and was typically 180-250 μL.

The raw titration data are sets of [Base volume, pH] data points that must be converted into equivalent sets of [pH, $\Sigma[A_i^-]$] points before abundances and acidities of acidic functional groups can be determined. This conversion procedure uses the electroneutrality equation for the titration as its starting point.

$$C_B + C_T + [H^+] = C_A + [OH^-] + \Sigma[A_i^-] \qquad (1)$$

In this equation, C_B and C_A represent initial strong base cations and anions that might be present in the sample and C_T is the concentration of added base titrant. As written, this equation assumes that there are no weak acids and bases other than the organic acids being titrated. Contamination by NH_3, H_2CO_3, H_4SiO_4, etc. would invalidate the equation and lead to erroneous estimates of the organic anion concentration. Concentrations of H^+ and OH^- were obtained from pH, using the Davies equation the estimate ionic strength at each point in the titration. This calculation is necessarily an approximate and iterative one, because the ionic strength of these dilute solutions is significantly affected by H^+ and OH^- at the lowest and highest pH values of the titrations and by $\Sigma[A_i^-]$ at intermediate pH values.

Carboxylic acid content was estimated as the value of $\Sigma[A_i^-]$ at pH 8.0, normalized to organic carbon concentration (μeq COOH/mg C). Other parameters were obtained by fitting titration data to the Gaussian distribution model of Perdue and coworkers (Perdue and Lytle, 1983; Perdue et al., 1984). In the Gaussian distribution model, it is assumed that the acid-base properties of an extremely complex mixture of organic acids can be represented by a continuum of acidic functional groups, the i^{th} of which is present at a concentration C_i and has a pK_a of pK_i. The probability of occurrence of an acidic functional group is related by a normal probability curve to the Gibb's free energy (or pK_a) for dissociation of that functional group.



In other words, within a "class" of acidic functional groups, those functional groups whose pK_a values are similar to the mean pK_a are far more likely to occur than are much stronger or weaker functional groups. In the preceding figure, the asterisks are a crude representation of the normal probability curve, which, in this model, is:

$$\text{Prob} = [1/(\sigma\sqrt{2\pi})] \exp[-0.5\,[(\mu - pK_a)/\sigma]^2\,] \tag{2}$$

The mole fraction of acidic functional groups in the interval [d pK_a] is the area of the enclosed rectangle in the figure, which is:

$$Ci/CL = \text{Prob} * [d\,pK_a] \tag{3}$$

Note that 68% of the area under the normal probability curve, and hence 68% of the acidic functional groups in the sample, lie within the pK_a interval of $[\mu-\sigma]$ to $[\mu+\sigma]$. Using this conceptual model, the acid-base properties of litter leachate organic acids are succinctly described by two classes of acidic functional groups, each of which is defined by its concentration, mean pK_a, and standard deviation of pK_a values around the mean (C, μ, and σ). The two classes of acidic functional groups are presumably carboxylic acids and phenols, although the phenol fraction probably includes other weak acids.

Modeling Gran Titration Estimates of Strong and Weak Acidity

In attempting to assess the short-term and long-term effects of acidic deposition on the titration alkalinities and/or acidities of lakes and streams, many authors have attempted to distinguish between "strong" and "weak" acids in natural water samples, the implication being that "strong" acids are a measure of atmospheric inputs of sulfuric and nitric acids. One of the most common analytical methods that is used for this purpose is the Gran function analysis of potentiometric titration data.

Several authors have demonstrated that dilute solutions of simple organic acids (especially relatively strong acids) cause conceptual problems in interpretation of Gran titration results (Barnard and Bisogni, 1985; Keene and Galloway, 1985). Similar problems are expected when the method is applied to water samples containing humic substances, such as surface waters or the litter leachate solutions. The computer simulations that have been conducted in this research make it possible to evaluate the performance of the Gran method in water samples containing a wide range of strong and weak acids and bases, including litter leachate organic acids.

The electroneutrality equation (1) can be further generalized by letting C_B represent all strong base cations (initial concentration plus added base titrant) and similarly letting C_A represent all strong acid anions. Dropping the C_T term, which is now a part of C_B, Eq. 1 can be rearranged to yield the Acid Neutralizing Capacity (ANC) of a solution:

$$ANC = C_B - C_A = \Sigma[A_i^-] + [OH^-] - [H^+] \qquad (4)$$

If the ANC equals zero, the pH of the solution is simply that of a pure solution of litter leachate organic acids ($\Sigma[HA_i]$). Negative or positive ANC values indicate solutions that contain excess strong acids and strong bases, respectively. A titration with strong acid or base simply changes the $[C_B - C_A]$ term, causing corresponding changes to occur on the right hand side of Eq. 4. When numerically generating titration data, it is far easier to systematically vary the right hand side of Eq. 4 and calculate the ANC term, assuming that the pH dependence of $\Sigma[A_i^-]$ is known or can be realistically modeled.

Acidity titrations are conducted by monitoring pH as strong base is added to a water sample (increasing C_B), and are exactly the opposite of alkalinity titrations, in which strong acid is added to a water sample (increasing C_A). The subsequent discussion focuses on acidity titrations, but is equally applicable to alkalinity titrations, which will not be further discussed. A Gran plot is simply a plot of $[H^+]$ or $[OH^-]$ vs. ANC, C_B, or C_A. At the simplest level, a Gran analysis assumes that, in the absence of weak acidity, one mole of H^+ will be neutralized for each mole of added OH^- in an acidity titration. Therefore, a plot of $[H^+]$ vs. ANC should have a slope of -1 up to the equivalence point of the titration. Beyond that point, the sample contains nothing to react with added base, so one mole of $[OH^-]$ will appear in solution for each mole of added base, and a plot of $[OH^-]$ vs. ANC will have a slope of + 1. Overall, the Gran plot of the acidity titration of a strong acid will thus consist of two straight lines that intersect the X-axis at a common point.

When a sample contains weak acids, the $[H^+]$ vs. ANC and $[OH^-]$ vs. ANC curves for an acidity titration do not intersect the X-axis at the same point, and, in fact, may not even be straight lines with slopes of -1 and +1. Even in such instances, the X-axis intercepts of the H^+ and OH^- Gran functions are still often interpreted as the Strong Acidity and Total Acidity of the sample, respectively. The Weak Acidity is then estimated as the difference between Total and Strong Acidity.

The principal complication in Gran function analysis of titration data for weak acid solutions arises because most common weak acids are appreciably ionized in dilute aqueous solutions. Dissociation of the weak acid causes significant non-linearity in the $[H^+]$ Gran curve and consequently prevents an accurate determination of Strong Acidity. The problem can be minimized to some extent by pre-acidification of the sample with a known quantity of strong acid to suppress dissociation of the weak acid. This remedy is most effective when applied to relatively concentrated solutions of relatively weak acids.

The mathematical description of the above phenomena can be rigorously derived for simple solutions of known weak acids for which the pH dependence of $\Sigma[A_i^-]$ in Eq. 4 can be expressed in terms of appropriate mass action laws and mass balance constraints. The complexity of the mixture of organic acids found in natural waters and litter leachate solutions is far too great for such rigorous approaches to be used. Rather, the pH dependence of $\Sigma[A_i^-]$ must be represented by some chemically-based model of the acid-base properties of such mixtures. The approach taken by Perdue and coworkers is known as the Gaussian distribution model (Perdue and Lytle, 1983; Perdue et al., 1984).

In the calculations that were done in this study, titration data were numerically generated for solutions containing various concentrations of strong acids, strong bases, and litter leachate organic acids. Data were generated at 0.1 pH intervals in the pH 3.0-11.0 range. The organic anion concentration $\Sigma[A_i^-]$ was calculated at each pH from the average Gaussian distribution model fitting parameters of litter leachate organic acids (see later results and discussion). The Gran functions for Total Acidity and Strong Acidity were computed using data from pH 3.0-4.0 and from pH 10.0-11.0, respectively.

RESULTS

Litter Leaching Experiments

The matrix of litter leaching experiments that was described in the **EXPERIMENTAL** section generated 660 leachate solutions (three replicates of 220 leaching experiments) which were analyzed for pH, total acidity [TotACY], total organic carbon [TOC], $[K^+]$, $[NH_4^+]$, $[Cl^-]$, $[NO_3^-]$, and $[SO_4^{2-}]$. The $[H^+]$ values were calculated from pH using an activity coefficient of 0.85. Weak acidity [WeakACY] was calculated as [TotACY] - $[H^+]$ - $[NH_4^+]$.

The following protocol was used to estimate the small number of data points that were missing in this data set. If two of three replicate measurements are available, their average is used for the missing value. If only one replicate is available, its value is used for both missing values. If all three replicates are missing, then each sample is independently estimated from adjacent data points in a leaching series. For example, in a typical experiment, where samples are leached every two days, data for a 4-day sample would be estimated as the average of the data for the 2-day and 6-day samples. Estimated values were neglected in calculation of averages, standard deviations, and cumulative yields.

The complete raw data set, including estimates of missing values that are given in square brackets, is given in Appendix A. Averages and standard deviations were computed from the three replicates of each experiment, and the results are given in Appendix B. This data set was corrected for the composition of initial leaching solutions and converted into units of μeq/kg litter (38 ml of leaching solution per 20 g of litter). Appendix C contains a cumulative data set that documents the effect of successive leachings of a sample. Raw data were corrected for the composition of initial leaching solutions, converted into units of μeq/kg litter, and then added to obtain the cumulative data set. The entire process of converting a raw data set into corrected average and cumulative data sets is illustrated in Table 1.

Table 1 includes the average initial compositions of the three leaching solutions (pH 5.6, 4.0, and 3.5). The pH 5.6 solution also contains 2 μeq/l of HCO_3^-. The tabulated values for *H* and *TotACY* were calculated assuming electroneutrality and that only H^+ and NH_4^+ are included in TotACY. Experimental measurements of *H* and *TotACY* were in generally good agreement with calculated values, the major exception being the *TotACY* of the pH 3.5 solution, which was only about 77% of the calculated value.

As anticipated, the heterogeneity of the litter and typical reproducibility problems associated with column leaching studies ultimately caused significant noise in the experiments. A further problem is thought to have arisen from time-dependent changes in the properties of the litter samples during the 18 months that were needed to conduct the experiments, even though the samples were refrigerated until used. To convey some general sense of the reproducibility of these experiments, the average, minimum, and maximum relative standard deviations for triplicate measurements of chemical parameters in all experiments are summarized in Table 2. Overall, the typical measured parameter was measured in triplicate with a standard deviation of about 23 percent.

Four major experiments were designed to evaluate the six previously identified factors that may influence the formation, mobilization, and transport of organic acids from forest soils to streams. While all experiments investigated the effect of forest litter type, the most complex experiment also studied the effects of litter temperature and leaching frequency. Separate experiments were conducted to isolate the effects of leaching solution pH, intensity of leaching events, and moisture content of litter between leachings. All experiments employed a cumulative leaching protocol, in which samples were leached at designated time intervals (usually 2-day intervals) for a total elapsed time of 6, 10, or 32 days. It is thus convenient to use Leaching Day as an independent variable for graphical representation of the results of all leaching experiments. A few selected plots that illustrate typical trends in raw, average, and cumulative data sets are given in Figures 4-6.

TABLE 1. Construction of Average and Cumulative Data From Raw Data

Leaching Solution (μeq/L)

Leach pH*	H	K	NH4	Cl	NO3	SO4	TotACY
5.6	2	2	12	12	12	11	14
4.0	109	2	12	12	46	86	121
3.5	338	2	12	12	124	237	350

Raw Data (μeq/L)

Day	H	K	NH4	Cl	NO3	SO4	TotACY
2	14.6	79	394	11	165	3	855
4	28.4	108	488	10	221	8	1386
6	33.6	108	443	14	256	11	1225
2	9.3	88	463	8	124	6	1104
4	11.6	121	562	4	104	9	1421
6	17.9	122	409	10	154	10	1200
2	12.7	56	421	9	129	6	920
4	15.9	87	403	6	146	10	1143
6	24.3	92	326	12	203	10	1020

Average Net Data (μeq/kg litter)

Day	H	K	NH4	Cl	NO3	SO4	TotACY
2	19.4	137	787	- 6	242	-12	1801
4	31.6	196	897	-10	276	- 4	2479
6	44.2	200	723	0	365	- 2	2159

Cumulative Net Data (μeq/kg Litter)

Day	H	K	NH4	Cl	NO3	SO4	TotACY
2	23.9	146	726	- 3	291	-15	1602
4	74.1	348	1630	- 7	688	-22	4212
6	134.1	549	2449	- 3	1151	-21	6517
2	13.9	163	857	- 8	213	-10	2075
4	32.1	390	1902	-23	388	-14	4752
6	62.3	618	2656	-27	657	-17	7009
2	20.3	103	777	- 6	222	-10	1725
4	46.7	264	1520	-18	477	-13	3874
6	89.1	435	2117	-19	840	-15	5789

* Only the pH 5.6 data were used in this example.

TABLE 2. Relative Standard Deviations of Chemical Measurements

Parameter	Relative Standard Deviation (%) Average	Minimum	Maximum
H^+	30	0	105
K^+	22	0	60
NH_4^+	19	3	56
Cl^-	24	2	109
NO_3^-	19	3	83
SO_4^{2-}	23	2	88
TotACY	18	2	58
WeakACY	27	4	131
TOC	25	0	139

TABLE 3. Coding Scheme Used In Bulk Litter Leaching Studies

Litter Type	Storage Conditions Temperature	Moisture	Leach Rate (cm/hr)	Leach pH
R = Red Spruce	H = 24°C	W = Wet	A = 0.25	A = 5.6
			B = 0.50	B = 4.0
N = Northern Hardwoods	C = 3°C	D = Dry	C = 1.00	D = H_2O
			D = 2.00	
			E = 4.00	

Example: RHWAA is a red spruce sample stored wet at 24°C and leached at 0.25 cm/hr with a synthetic rain of pH 5.6.

Figure 4

Raw Weak Acidity Versus Leach Day
Red Spruce Leaching Frequency Study

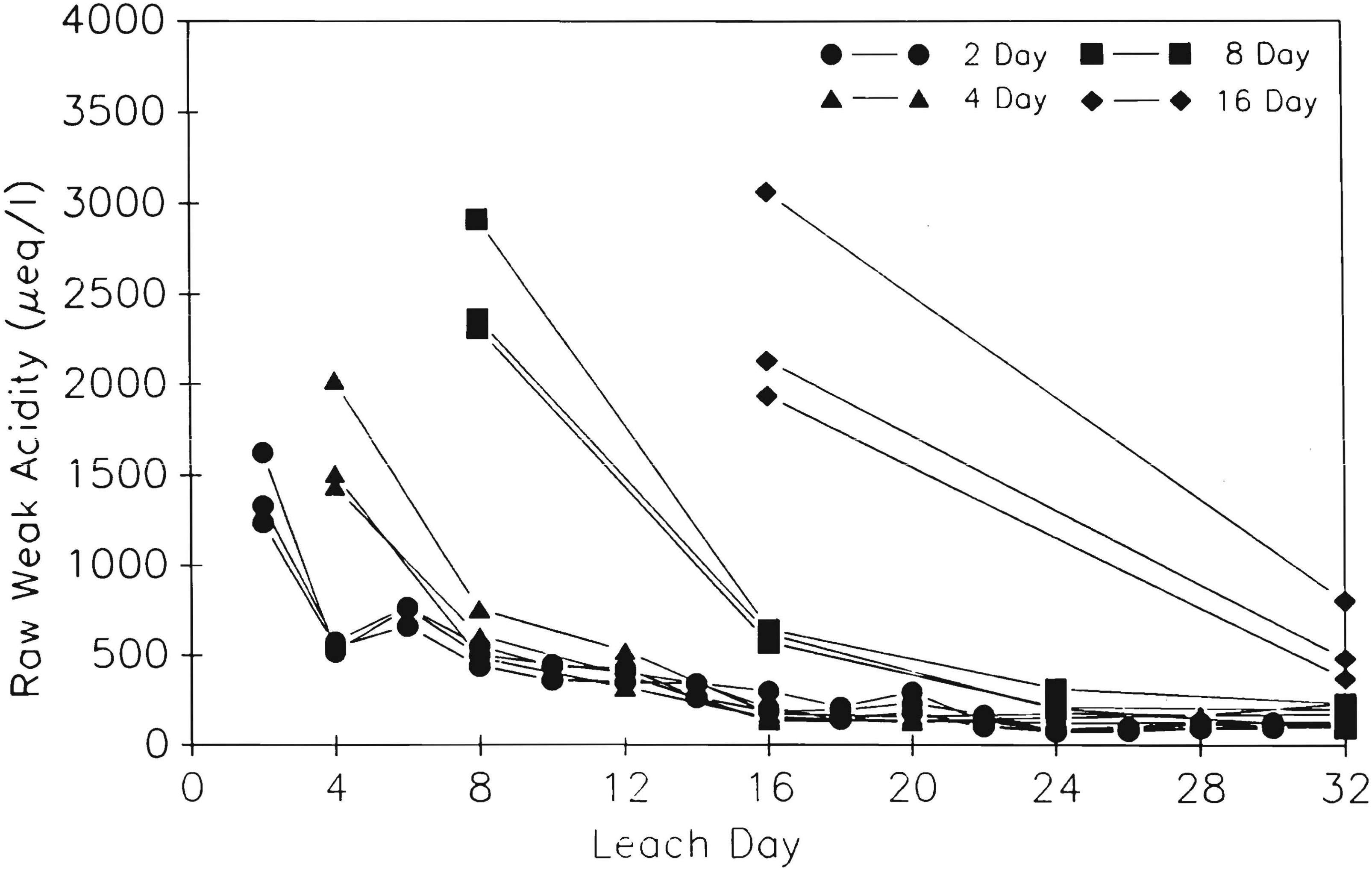
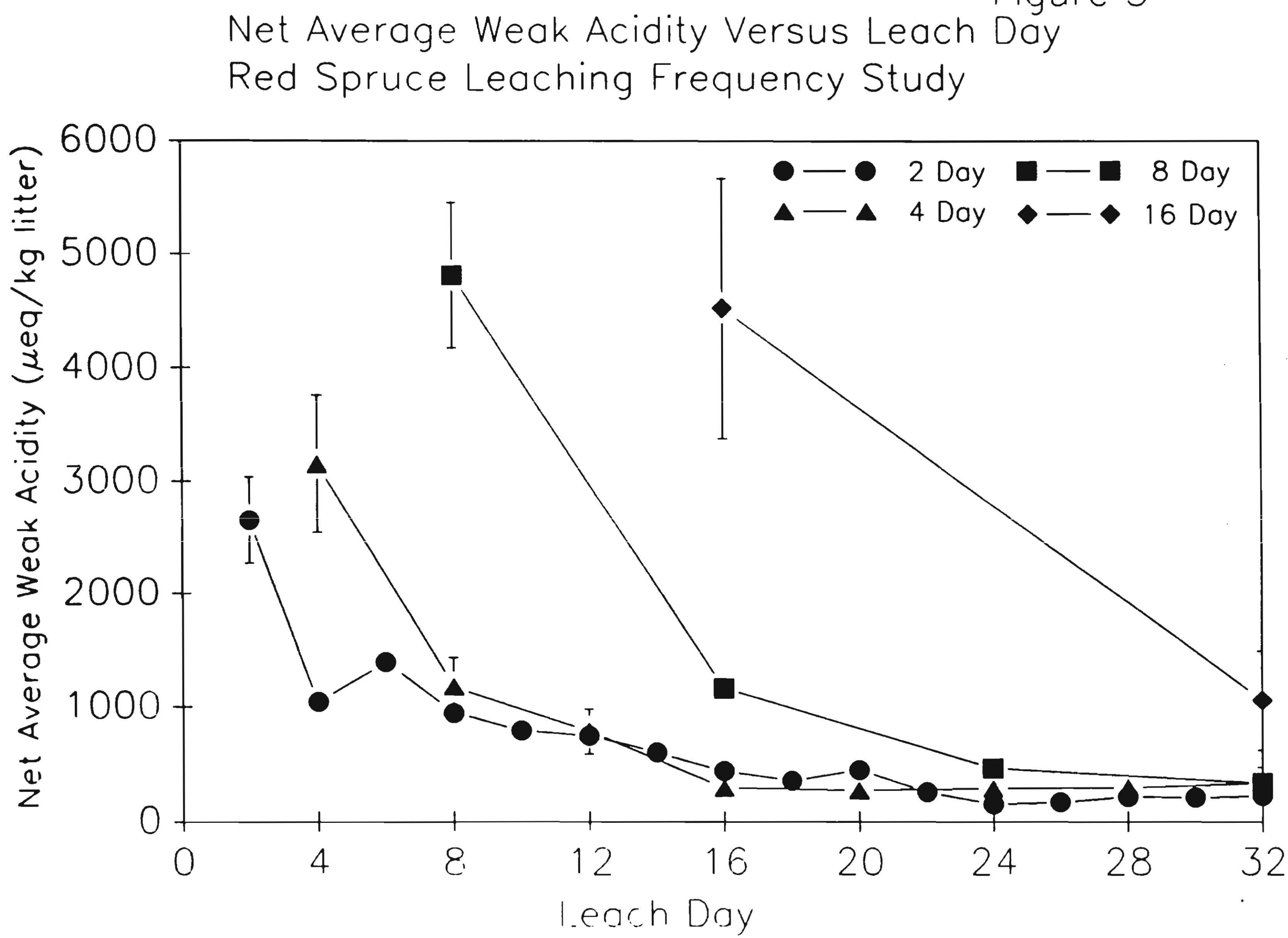
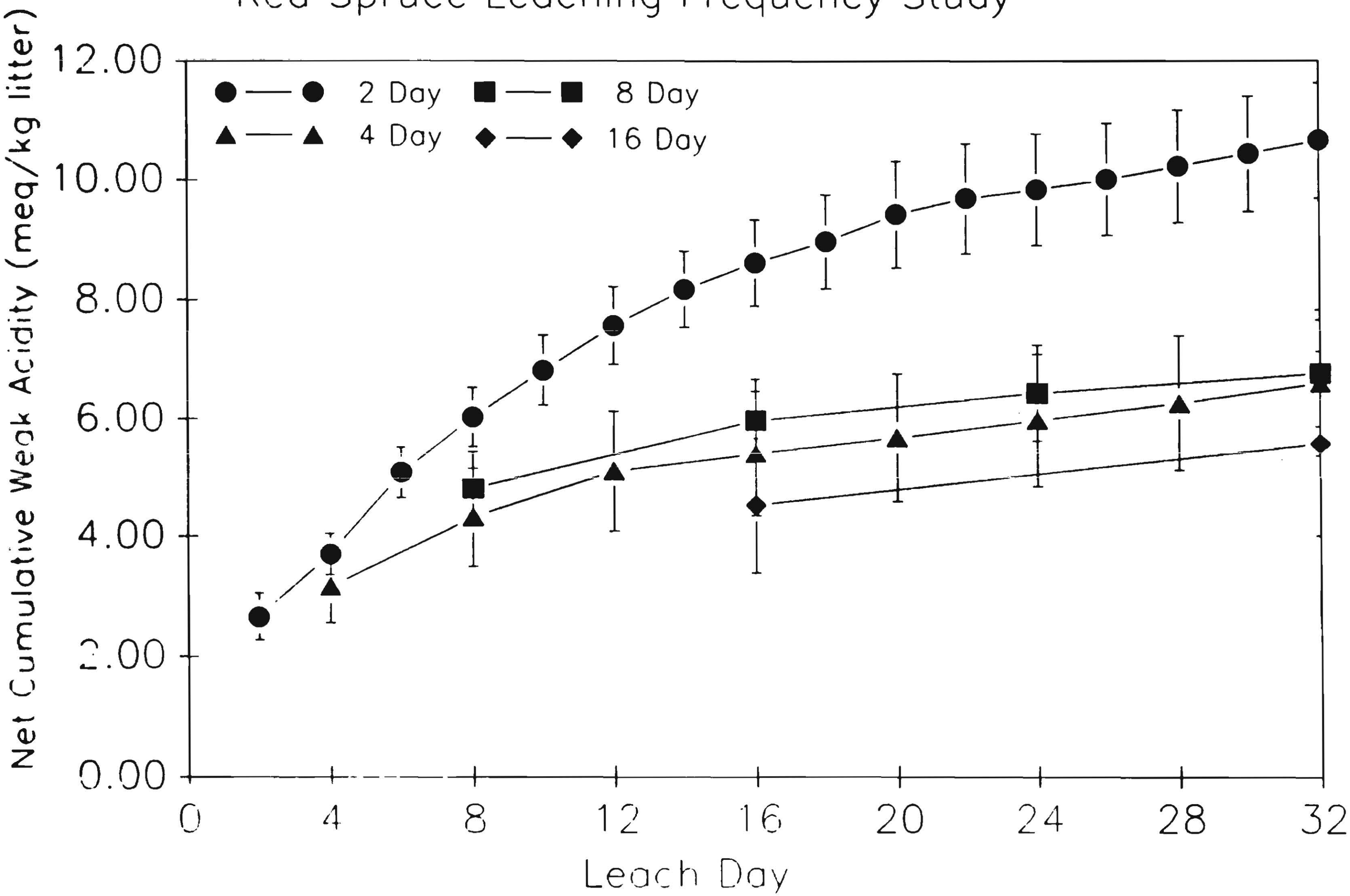


Figure 5



Net Average Weak Acidity Versus Leach Day
Red Spruce Leaching Frequency Study
Net Average Weak Acidity (μeq/kg litter)
6000
5000
4000
3000
2000
1000
0
2 Day
8 Day
4 Day
16 Day
0
4
8
12
16
20
24
28
32
Leach Day

Figure 6
Net Cumulative Weak Acidity Versus Leach Day
Red Spruce Leaching Frequency Study



Isolation and Characterization of Leachate Organic Acids

A number of litter leachate organic matter samples were isolated from bulk litter leaching experiments. To facilitate the presentation of results and subsequent discussion of these samples, a sample coding protocol is introduced in Table 3.

Isolation and Preparation

The extracted and isolated amounts of dissolved organic carbon (calculated from DOC x Volume) in each bulk leaching experiment are presented in Table 4. The yields and percent recoveries vary greatly between experiments. We observed that the highest yields were obtained on fresh litter samples, suggesting that some type of alteration occurred during sample storage. Percent recoveries averaged 68% (Table 4), indicating a 32% loss of DOC in the isolation/purification scheme. Nonetheless, our DOC recoveries were generally better than the 30-50% recoveries obtained by adsorption of DOC on XAD-8 resin (Thurman and Malcolm, 1981). DOC losses during cation exchange and ultrafiltration of a typical sample (Table 5) are consistent with the average recovery of 68% given in Table 4 and suggest that most of our DOC loss occurs during ultrafiltration.

Extraction methodology was not a major component of this project and will not be discussed in the following section of the report. Nevertheless, it is worth noting that low molecular weight compounds are preferentially lost in our ultrafiltration procedure, while hydrophilic polar compounds are preferentially lost in the XAD resin procedure. The two methodologies would therefore be expected to yield different fractions from a common starting sample. We believe that the loss of low molecular weight compounds is less detrimental than the loss of polar compounds in this particular study, where the emphasis is on acidic functional groups. Furthermore, Shuman (1990) has suggested that the isolation of DOM by adsorption on XAD resins may result in isolated samples with very similar chemical properties, regardless of sample origin. For these reasons and the greater overall recoveries of DOC, we believe that the ultrafiltration procedure yields a more representative fraction of the original litter leachate organic matter.

TABLE 4. Carbon Balance During Isolation of Bulk Litter Leachate Samples

Sample	Extracted mg C	Isolated mg C	Percent Recovery
NHWBA	116	75	65
RCWCA	30	21	70
RHWAA	240	178	71
RHWDA			
NHWCA	31	14	45
NHWAA	54	38	70
NHWCB	54	15	27
NCWCA	43	30	70
RHWCD	179	109	57
NHWCD	128	88	65
RHWBA	91	68*	74
RHWCA	360	344*	96
RHWCB	120	64*	53
RHWEA	106	81*	76
RHDCA	52	56*	108
Average	115	84	68
Std Dev	93	86	20
Maximum	360	344	108
Minimum	30	14	27

* Carbon yield was calculated from the yield of isolated product and its elemental composition rather than from DOC concentration and solution volume.

TABLE 5. Complete Carbon Balance For the NHWBA Bulk Leachate Sample

Process	DOC Recovered mg C	%
Initial	116	100
Cation Exchange	103	89
Ultrafiltration		
Initial step	86	74
1st HCL wash	81	70
2nd HCL wash	79	68
3rd HCL wash	77	66
4th HCL wash	74	64
5th HCL wash	72	62

Freeze-dried litter leachate organic matter samples were analyzed for carbon, hydrogen, nitrogen, and ash, and oxygen was calculated by difference as %O = [100-%C-%H-%N-%Ash]. Atomic H/C, N/C, and O/C ratios were then calculated to examine how the elemental compositions differ from their parent materials and how they vary with leaching conditions. Table 6 presents these data and comparable data for the Raven Fork Creek DOC sample.

TABLE 6. Average C,H,N Analyses of Litter Leachate Organic Matter and Raven Fork Creek Dissolved Organic Matter

Sample	% C	% H	% N	% Ash	H/C	O/C	N/C
RHWCA	46.84	5.84	3.65	8.58	1.50	0.70	0.067
RHWCB	42.99	5.50	2.89	13.51	1.54	0.85	0.058
RHWAA	45.74	4.87	1.88	2.80	1.28	0.78	0.035
RHWBA	44.51	5.20	2.91	4.22	1.40	0.80	0.056
RHWDA	46.01	5.42	2.83	4.76	1.41	0.75	0.053
RHWEA	46.20	5.43	3.24	5.57	1.41	0.73	0.060
RHDCA	46.11	5.58	3.52	6.51	1.45	0.73	0.065
NHWEA	46.04	5.00	2.25	9.27	1.30	0.76	0.042
NHWAA	46.96	4.82	1.97	8.82	1.23	0.74	0.036
RHWCD	45.97	4.83	2.28	3.18	1.26	0.77	0.042
NHWCD	46.26	5.06	2.74	6.14	1.31	0.74	0.051
Average	45.78	5.23	2.74	6.67	1.37	0.76	0.051
Std Dev	1.07	0.33	0.57	3.02	0.10	0.04	0.011
Raven Fork Creek DOM	52.30	5.09	0.44	28.03	1.17	0.60	0.007

C, H, and N percentages are on a dry, ash-free basis.

<u>Functional Group Analysis</u>

Estimates of carboxyl group content and total acidity of these samples were obtained by titrations with standard KOH solution, as described in the **EXPERIMENTAL** section. To provide more insight into the nature of the data manipulations described there, an illustrative example for a subset of titration data points is given in Table 7. It is evident that the buffer contamination problem was minor.

TABLE 7. Example Titration Data Subset For Sample RHWBA

Initial pH	Corrected pH	Initial $\Sigma[A_i^-]$	Corrected $\Sigma[A_i^-]$
3.537	3.543	2.96E-04	2.92E-04
3.994	3.991	6.49E-04	6.49E-04
4.472	4.462	9.05E-04	9.06E-04
5.047	5.029	1.21E-03	1.21E-03
6.086	6.054	1.74E-03	1.74E-03
7.003	6.960	2.17E-03	2.17E-03
8.068	8.012	2.61E-03	2.61E-03
9.162	9.092	3.13E-03	3.13E-03
9.751	9.673	3.52E-03	3.52E-03
9.984	9.903	3.69E-03	3.70E-03
10.263	10.178	3.92E-03	3.93E-03
10.504	10.416	4.10E-03	4.12E-03
10.726	10.634	4.30E-03	4.33E-03
10.994	10.897	4.77E-03	4.83E-03
11.035	10.937	4.88E-03	4.94E-03
11.052	10.953	4.94E-03	5.00E-03
11.083	10.983	5.06E-03	5.13E-03
11.113	11.012	5.18E-03	5.25E-03

The bimodal Gaussian distribution model was fit to the corrected experimental data (-Log[H^+], $\Sigma[A_i^-]$) to determine the best values of C, μ, and σ for each class of binding sites. As previously indicated, the concentration of the first class of binding sites (carboxyl groups) was determined directly from titration data and held constant throughout the regression calculations. The average fitting parameters for each litter leachate sample and the Raven Fork Creek DOM sample are given in Table 8. To facilitate subsequent modeling calculations, an overall average set of C, μ, and σ values for each class of proton binding sites in litter leachate samples was computed. If any average fitting parameter of a sample was a statistical outlier according to the 4d test, that sample was excluded from the overall averaging process. There was far greater consistency in estimation of the fitting parameters for carboxyl groups than for weakly acidic groups, both within and between samples. Fortuitously, in natural waters, pH usually ranges between six and nine (Stumm and Morgan, 1981), so the weaker class of acidic functional groups is unlikely to dissociate

TABLE 8. Gaussian Distribution Model Fitting Parameters for the Acidic Functional Groups of Litter Leachate Organic Acids and Raven Fork Creek DOM

		Carboxylic Acids			Other Weak Acids		
Sample	N	μeq/mg C	μ	σ	μeq/mg C	μ	σ
RHWCA	2	4.14 ± 0.00	4.68 ± 0.10	1.55 ± 0.11	3.19 ± 0.04	11.39 ± 0.67	1.97 ± 0.58
RHDCA	3	3.70 ± 0.09	5.09 ± 0.31	1.62 ± 0.47	2.71 ± 0.42	10.09 ± 0.41	1.34 ± 0.52
RHWCB	3	7.91 ± 0.09	4.36 ± 0.09	2.18 ± 0.07	3.02 ± 0.77	9.34 ± 0.47	1.09 ± 0.38
RHWDA	3	3.76 ± 0.04	5.18 ± 0.01	1.40 ± 0.05	4.16 ± 2.34	10.77 ± 1.11	1.53 ± 0.62
RHWEA	3	3.92 ± 0.08	5.21 ± 0.06	1.41 ± 0.02	4.81 ± 1.15	10.74 ± 0.51	1.43 ± 0.24
NHWCD	3	6.45 ± 0.16	4.33 ± 0.02	2.10 ± 0.05	3.14 ± 1.39	9.59 ± 0.27	1.04 ± 0.14
NHWCA	1	5.48	5.25	1.12	2.98	9.63	0.73
RCWCA*	1	7.09	5.13	1.16	433.00	14.40	1.73
RHWBA*	3	5.21 ± 0.12	5.33 ± 0.08	1.56 ± 0.02	30.91 ± 0.16	13.31 ± 0.07	2.16 ± 0.04
RHWAA*	6	5.06 ± 0.09	4.54 ± 0.09	2.12 ± 0.23	11.80 ± 5.90	12.69 ± 1.08	2.47 ± 0.15
RHWCD*	2	6.27 ± 0.22	4.46 ± 0.14	2.28 ± 0.12	12.00 ± 1.99	12.93 ± 0.17	1.98 ± 0.48
NHWAA*	2	5.33 ± 0.47	5.03 ± 0.19	1.27 ± 0.02	13.87 ± 9.73	11.90 ± 1.34	1.66 ± 0.22
NHWBA*	4	7.52 ± 1.47	3.82 ± 0.19	2.47 ± 0.10	8.30 ± 4.37	11.24 ± 0.83	2.37 ± 0.56
Average Leachate		5.05 ± 1.51	4.87 ± 0.38	1.62 ± 0.36	3.43 ± 0.70	10.22 ± 0.70	1.30 ± 0.37
Raven Fork Creek DOM	3	4.48 ± 0.40	3.02 ± 0.17	1.83 ± 0.30	2.60 ± 0.78	9.29 ± 0.68	2.07 ± 0.71

* At least one of the fitting parameters for this sample can be rejected statistically with the 4d test, so the sample is not included in the overall average set of model fitting parameters.

to an appreciable extent. This is even more true in acid-impacted waters with pH values of less than six. The carboxyl groups, in contrast, will be largely dissociated at pH values of five or greater, and they are expected to significantly influence the acid-base chemistry of natural waters.

<u>Modeling Gran Titration Estimates of Strong and Weak Acidity</u>

Base titrations of average litter leachate samples were simulated using the average Gaussian distribution model fitting parameters in Table 8 to describe the relative concentrations and acidic strengths of the litter leachate organic acids. The results at DOC concentrations of 1-32 mg/L are summarized in Table 9, which compares the actual composition of each solution with the predictions of Gran plots for "strong", "weak", and "total" acidity.

TABLE 9. Gran Function Analysis of Raven Fork Organic Acid Titration Data

DOC	Actual Acidity (μeq/L)				Gran Acidity (μeq/L)		
(mg/L)	Mineral	Carboxyl	Phenolic	Total	Strong	Weak	Total
1.0	0.0	5.0	3.4	8.4	1.5	5.1	6.6
2.0	0.0	10.1	6.8	16.9	3.0	10.2	13.2
4.0	0.0	20.2	13.6	33.8	6.0	20.5	26.5
8.0	0.0	40.4	27.2	67.6	12.0	41.0	53.0
16.0	0.0	80.8	54.4	135.2	24.0	81.9	105.9
24.0	0.0	121.2	81.6	202.8	36.0	122.8	158.8
32.0	0.0	161.6	108.8	270.4	48.0	163.8	211.8

DISCUSSION

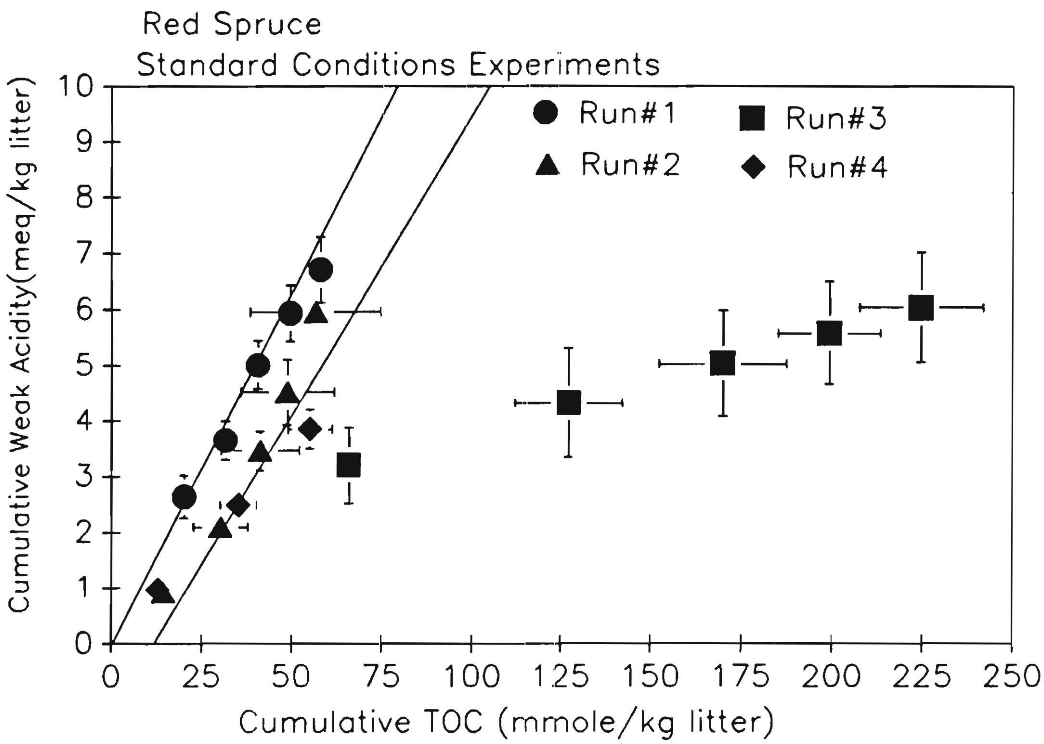
Statistical Considerations

Because the focus of this study was the investigation of the nature and amount of organic acidity mobilized from forest litter, the discussion of the small scale leaching studies will focus on weak acidity and total organic carbon data. It can be assumed that the ratio of WeakACY to TOC provides a maximum estimate of the carboxylic acid (COOH) content of the dissolved organic matter. To distinguish this upper limit from the actual COOH, the symbol $COOH^*$ will be employed.

As stated previously in the **RESULTS** section, problems associated with changes in the litter over time severely hamper the interpretation of both small scale and bulk litter leaching results. "Standard conditions" leaching experiments (pH 5.6, 1 cm/hr, 24 °C, stored wet for 2 days between leachings) were run in triplicate as a control for each of the leaching parameters investigated. Changes in characteristics of the litter over the one-and-a-half year period of the study are suggested by statistical analysis of the data collected in the "standard conditions" leaching experiments. When evaluating the potential effect of an experimental leaching parameter on the composition of leachate solutions, comparisons will be made to the "standard conditions" experiments and their inherent variance.

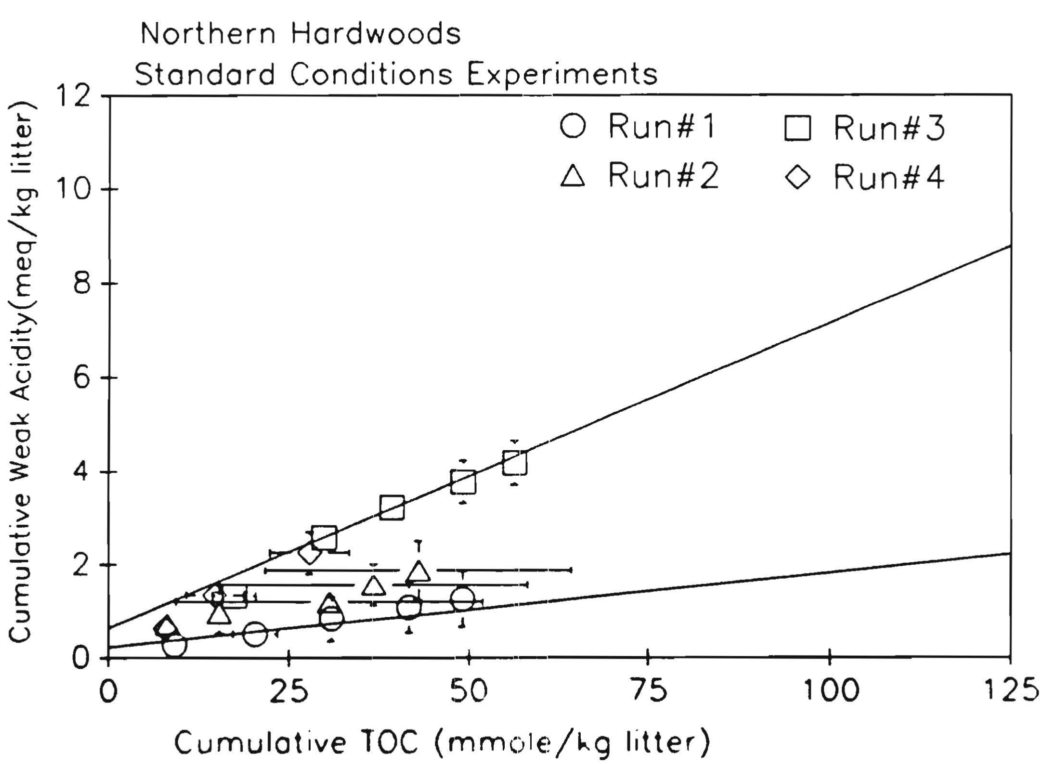
To obtain average values and standard deviations for WeakACY and TOC in the "standard conditions" experiments and in experiments in which experimental leaching parameters are being manipulated, it is necessary to directly examine raw data sets. Cumulative data sets (Appendix C) were therefore calculated for all complete experiments (those with no missing data points in the raw data sets). Average values and standard deviations ($N=3$) for cumulative WeakACY and TOC data for the four "standard conditions" leaching experiments are plotted for Red Spruce and Northern Hardwoods litters in Figures 7 and 8, respectively.

Fig . 7



Red Spruce
Standard Conditions Experiments
Run#1
Run#2
Run#3
Run#4
Cumulative Weak Acidity(meq/kg litter)
Cumulative TOC (mmole/kg litter)
0
1
2
3
4
5
6
7
8
9
10
0
25
50
75
100
125
150
175
200
225
250

Fig. 8



Northern Hardwoods
Standard Conditions Experiments
Run#1
Run#2
Run#3
Run#4
Cumulative Weak Acidity(meq/kg litter)
Cumulative TOC (mmole/kg litter)
0
2
4
6
8
10
12
0
25
50
75
100
125

By combining all "standard conditions" data sets for each litter type into one composite set, the overall standard deviations in cumulative WeakACY and TOC at each leaching day were calculated (neglecting the data from the Red Spruce pH study, which differ markedly from all other standard conditions data). The solid straight lines in the plots define an approximate ± 1 standard deviation "window" whose borders encompass the observed range in standard deviations of both variables.

For an experimental leaching parameter to have a statistically significant effect on leachate solution composition, the resulting cumulative WeakACY and/or TOC data must lie outside the ± 1 standard deviation "window". Even though the results of a non-"standard conditions" experiment may be insignificant according to these criteria, those results may differ by more than ± 1 standard deviation from the results of the simultaneously conducted "standard conditions" experiment. Because we are not certain of the nature or extent of long-term variations in litter properties, we will identify and discuss such experimental results.

Litter Leaching Experiments

Forest Litter Type

Both Red Spruce (RS) and Northern Hardwoods (NH) litters were used in all experiments and the detailed effects of litter type will be included in the discussion of the effects of other experimental parameters. As a general observation, leachate solutions derived from RS litter have higher WeakACY and TOC values than those from NH litter. Interestingly, $COOH^*$, which is the ratio WeakACY/TOC, is about the same under the leaching conditions of this study for RS and NH litter leachate organic acids.

Litter Temperature

The effects of storage temperature and leaching frequency on litter leachate solution chemistry were investigated simultaneously by storing litter samples at either 24 °C or 3 °C between leachings at either 2, 4, 8, or 16 day intervals. At a given temperature, higher cumulative WeakACY and $COOH^*$ values were usually obtained from RS litter than from NH litter samples, with both litter types yielding similar cumulative TOC concentrations.

For RS litter samples, both cumulative WeakACY and cumulative TOC were lower at 3 °C than at 24 °C, regardless of leaching frequency (Figs. 9 and 10). The $COOH^*$ values of RS leachate solutions are slightly higher at the higher temperature for all leaching frequencies. For NH litter samples, while both cumulative WeakACY and cumulative TOC are generally somewhat lower at 3 °C, there is little difference in $COOH^*$ values of samples leached at 24 °C and 3 °C, regardless of leaching frequency (Figs. 11 and 12). The reduction in cumulative TOC and cumulative WeakACY at 3 °C is consistent with a decrease in microbial activity at the lower temperature. In summary, while cumulative WeakACY and TOC values are lower at lower temperature, $COOH^*$ values are relatively invariant for both litter types.

Moisture Content of Litter

The effect of moisture content during storage of litter samples on litter leachate solution chemistry was investigated by air-drying litter samples before storing between leachings (see Figs. 13-14). Under standard (i.e., moist) conditions, higher cumulative WeakACY and $COOH^*$ values were obtained from RS litter than from NH litter samples, with both litter types yielding similar cumulative TOC concentrations. However, under dry and presumably much more aerobic conditions, much greater cumulative WeakACY values and greater $COOH^*$ values are obtained from NH litter, with similar cumulative TOC values being obtained from both litters.

For both litter samples, significantly higher cumulative TOC values are obtained under dry conditions. However, cumulative WeakACY values are higher under dry conditions only for the NH litter sample. The net effect of these changes in cumulative WeakACY and cumulative TOC under dry conditions is greatly increased $COOH^*$ values for NH litter leachate samples and a slight decrease in $COOH^*$ values for RS litter leachate samples. At the watershed level, these results suggest that greater export of organic

Fig. 9

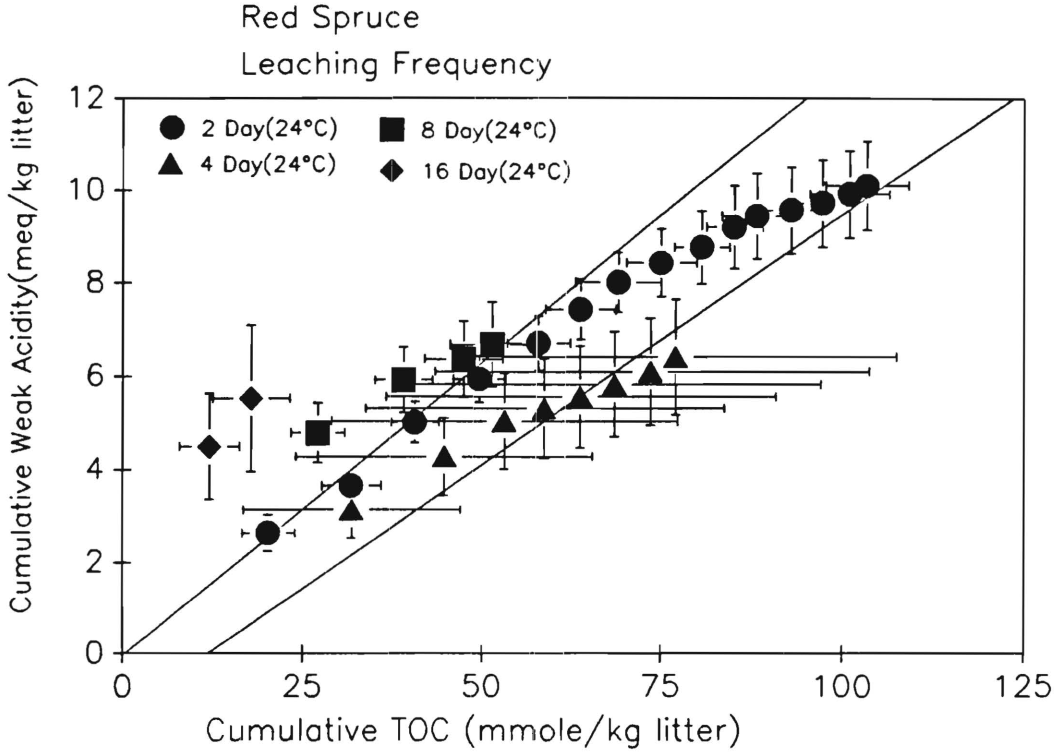

Red Spruce
Leaching Frequency
2 Day(24°C)
4 Day(24°C)
8 Day(24°C)
16 Day(24°C)
Cumulative Weak Acidity(meq/kg litter)
Cumulative TOC (mmole/kg litter)
0
2
4
6
8
10
12
0
25
50
75
100
125

Fig. 10

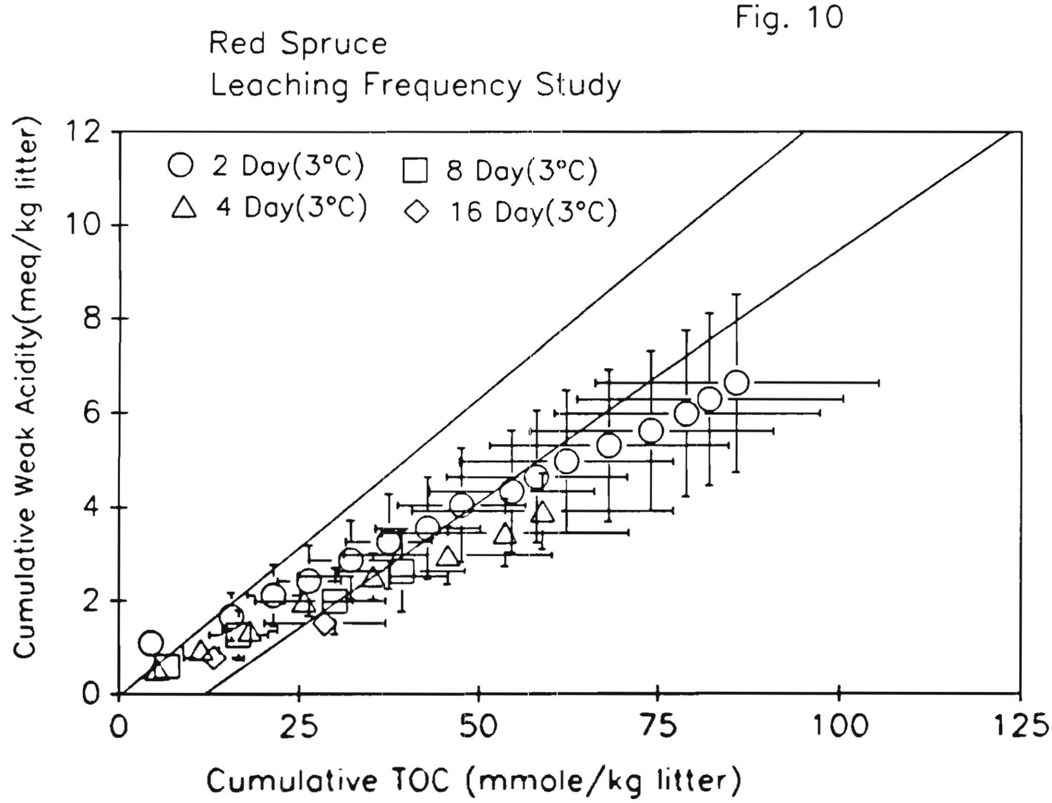

Red Spruce
Leaching Frequency Study
2 Day(3°C)
4 Day(3°C)
8 Day(3°C)
16 Day(3°C)
Cumulative Weak Acidity(meq/kg litter)
Cumulative TOC (mmole/kg litter)
0
2
4
6
8
10
12
0
25
50
75
100
125

Fig. 11

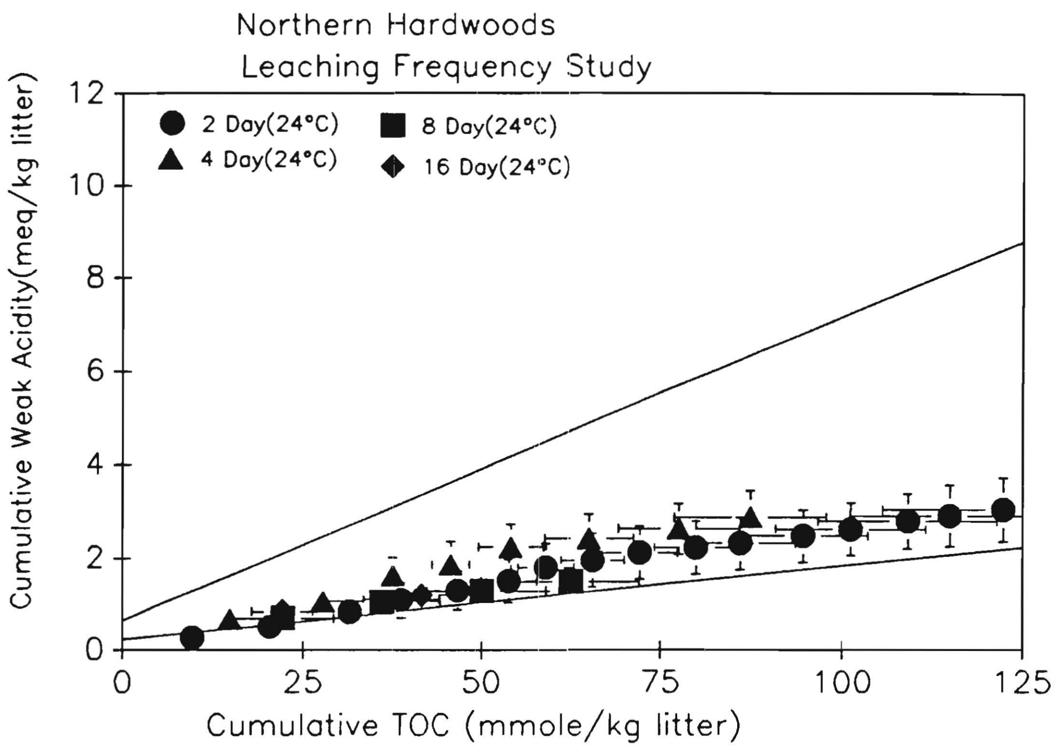

Northern Hardwoods
Leaching Frequency Study
2 Day(24°C)
4 Day(24°C)
8 Day(24°C)
16 Day(24°C)
Cumulative Weak Acidity(meq/kg litter)
0
2
4
6
8
10
12
0
25
50
75
100
125
Cumulative TOC (mmole/kg litter)

Fig. 12

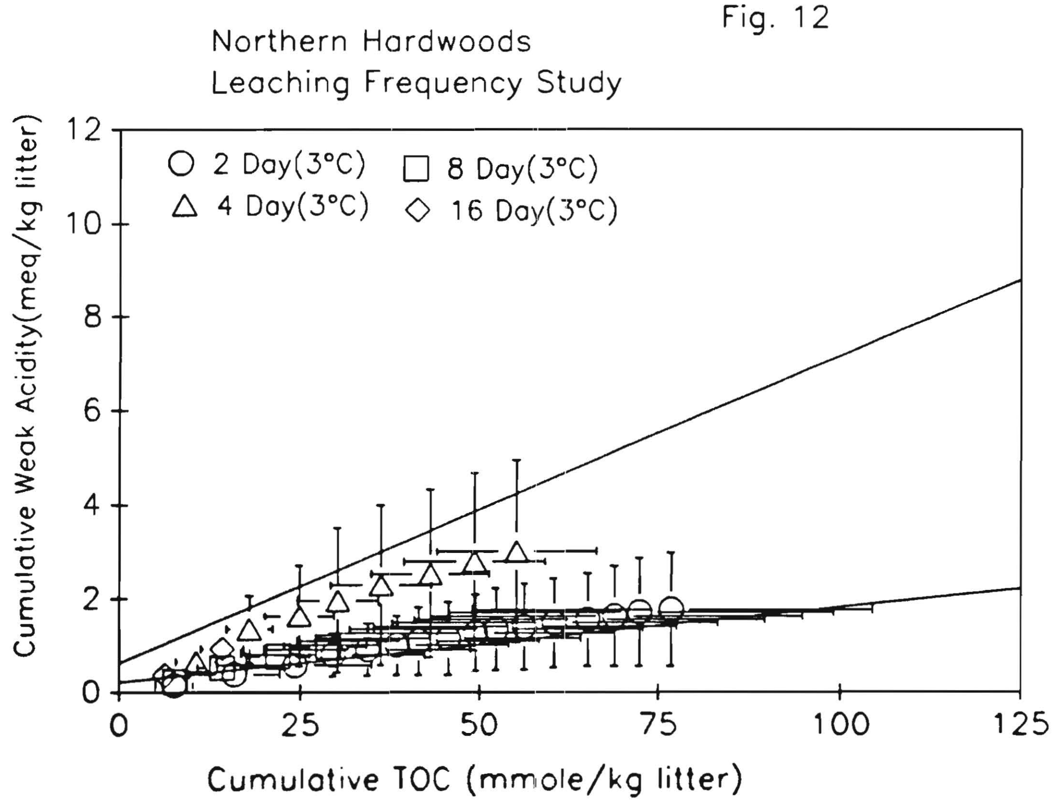

Northern Hardwoods
Leaching Frequency Study
2 Day(3°C)
4 Day(3°C)
8 Day(3°C)
16 Day(3°C)
Cumulative Weak Acidity(meq/kg litter)
0
2
4
6
8
10
12
0
25
50
75
100
125
Cumulative TOC (mmole/kg litter)

Fig. 13

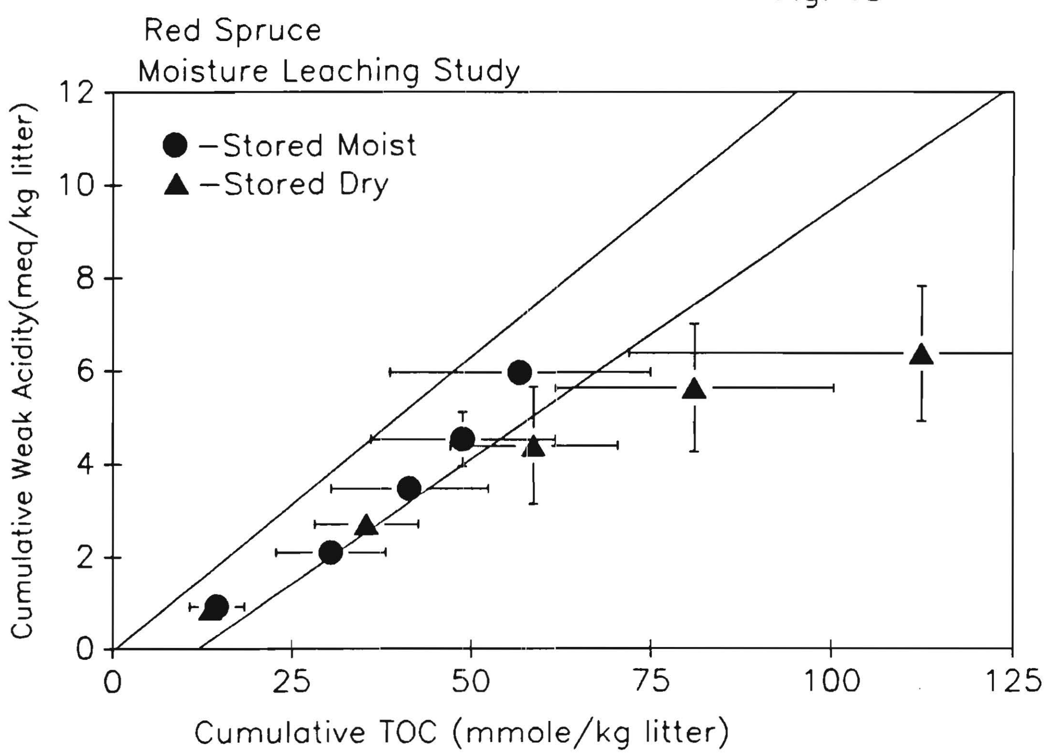
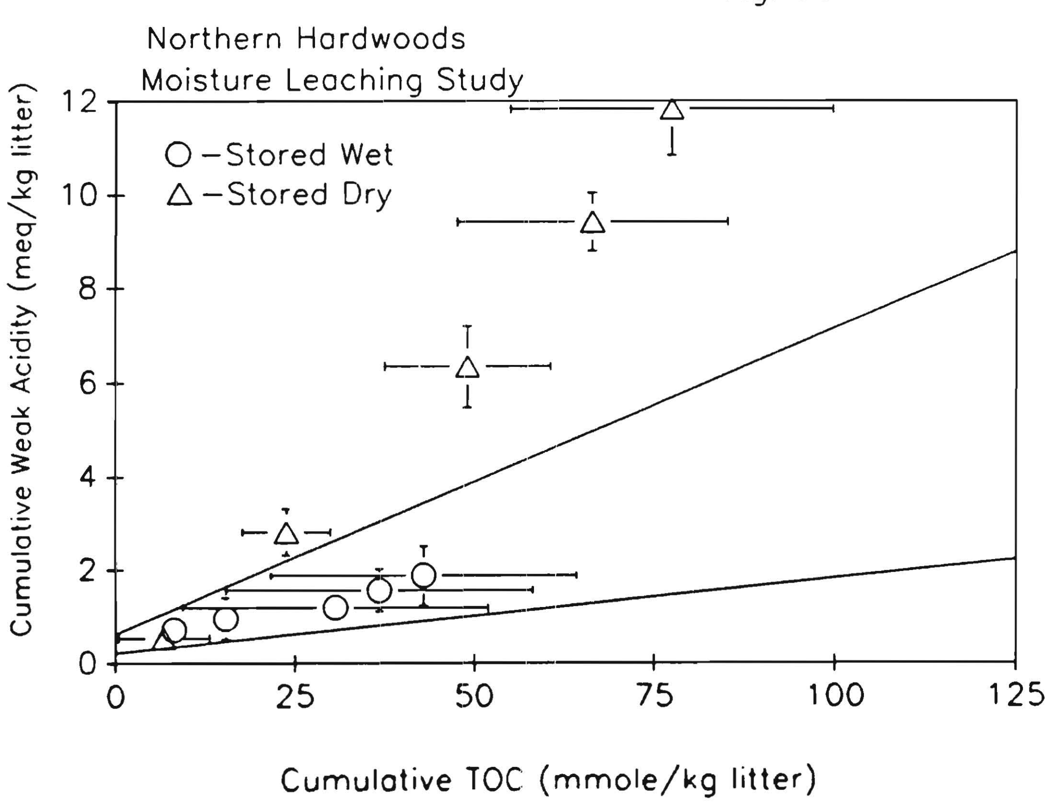

Red Spruce
Moisture Leaching Study
● –Stored Moist
▲ –Stored Dry
Cumulative Weak Acidity(meq/kg litter)
0
2
4
6
8
10
12
0
25
50
75
100
125
Cumulative TOC (mmole/kg litter)

Fig. 14


Northern Hardwoods
Moisture Leaching Study
○ –Stored Wet
△ –Stored Dry
Cumulative Weak Acidity (meq/kg litter)
0
2
4
6
8
10
12
0
25
50
75
100
125
Cumulative TOC (mmole/kg litter)

carbon (but not necessarily organic acids) will occur in a drier, more oxidizing forest litter environment.

pH of Leaching Solution

The effect of the pH of leaching solutions on organic matter mobilization and acidic strength was examined by leaching both under standard conditions (i.e., pH 5.6) and at pH values of 4.0 and 3.5. The results (Figs. 15-16) summarize the effect of the pH of the leaching solution on cumulative WeakACY, cumulative TOC, and COOH* values of the leachate solutions. For RS litter samples, the cumulative TOC values obtained under "standard conditions" in this pH study differ greatly from the results of other "standard conditions" experiments, so no overall significance can be given to these results (Fig. 7 (Run #3) and Fig. 15). The high cumulative TOC values observed in this study, which was the first set of leaching experiments carried out, is consistent with changes in litter quality with time and the general trend of higher cumulative TOC values in the earlier studies. Whatever the cause of such high cumulative TOC values in the RS experiments, it is inappropriate to compare these results with those obtained on NH litter samples, where the "standard conditions" experiment is consistent with other such experiments (Fig. 8 (Run #3) and Fig. 16).

Even if the disparity between these and other experiments on RS litter samples is ignored and only the three pH experiments are compared, virtually no effect of the pH of the leaching solution is observed for cumulative WeakACY, cumulative TOC, or COOH* values. Similarly, all pH experiments for NH litter samples fall within the standard conditions "window" for that sample (Fig. 16). On the basis of these observations, it is unlikely that the pH of rainfall will significantly affect the production or mobilization of organic carbon and organic acids in forest litter horizons. This study does not consider, however, the possibility that the passage of mobilized organic matter through mineral soil horizons might be affected by the pH of rainfall, with consequent effects on overall export of organic matter into surface waters.

Fig. 15

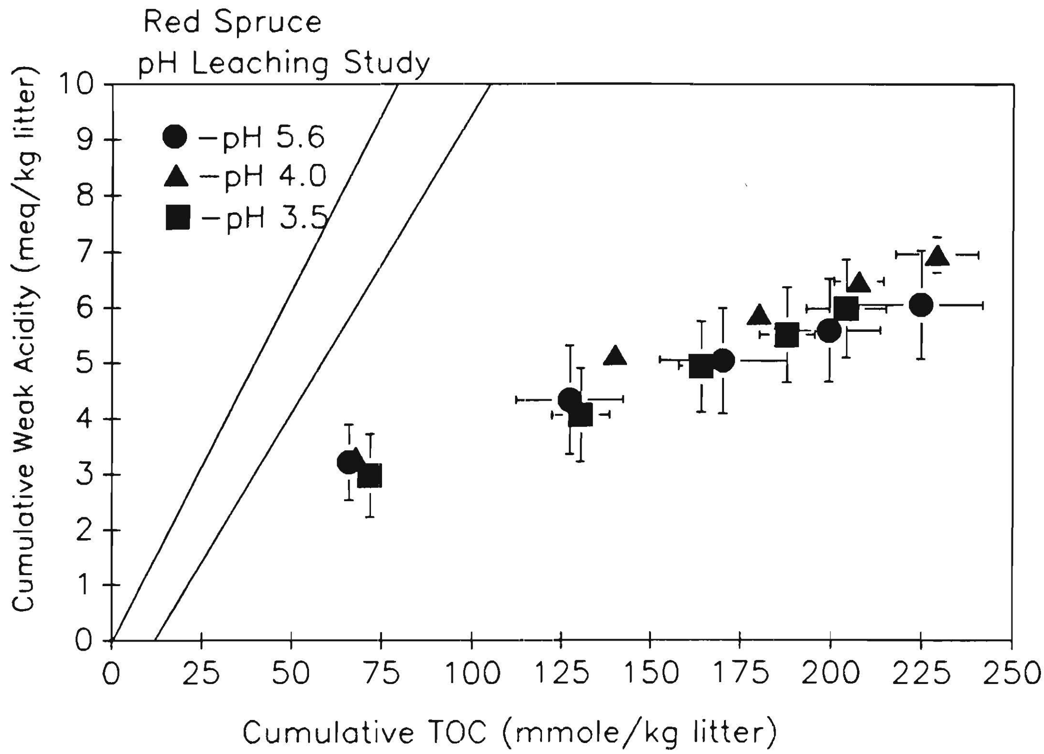
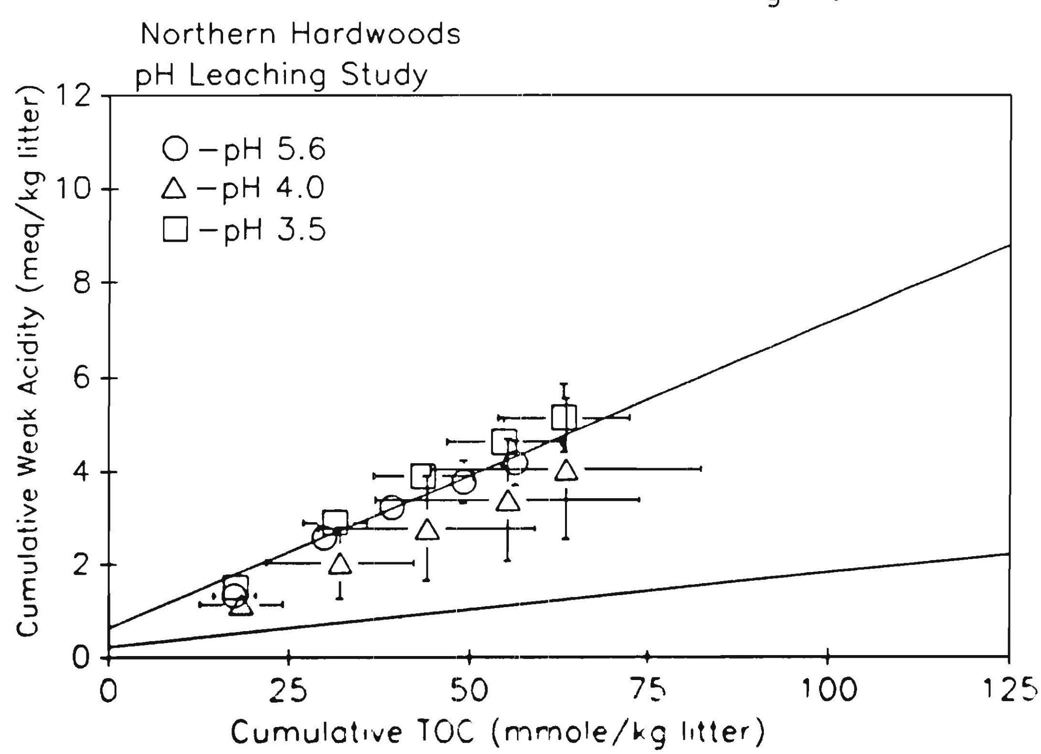

Red Spruce
pH Leaching Study
●–pH 5.6
▲–pH 4.0
■–pH 3.5
Cumulative Weak Acidity (meq/kg litter)
0
1
2
3
4
5
6
7
8
9
10
0
25
50
75
100
125
150
175
200
225
250
Cumulative TOC (mmole/kg litter)

Fig. 16


Northern Hardwoods
pH Leaching Study
○–pH 5.6
△–pH 4.0
□–pH 3.5
Cumulative Weak Acidity (meq/kg litter)
0
2
4
6
8
10
12
0
25
50
75
100
125
Cumulative TOC (mmole/kg litter)

Frequency of Leaching Events

The effects of leaching frequency and storage temperature on litter leachate solution chemistry were investigated simultaneously by storing litter samples at either 24 °C or 3 °C between leachings at either 2, 4, 8, or 16 day intervals (see prior discussion of temperature effects and Figs. 9-12). As might be expected, the more times a litter sample is leached in a given time period (e.g., 32 days), the greater the yields of cumulative WeakACY and cumulative TOC. All other factors being constant, a watershed that receives frequent rainfall would be expected to annually export more organic acids to surface waters. However, any biological effects of organic acids are likely to be related to their instantaneous concentrations in surface waters, not their annual export. The data in Appendices A-C show that infrequently leached litter samples have much higher WeakACY and TOC values. A watershed that receives infrequent heavy rainfall is thus expected to export much higher instantaneous concentrations of organic acids.

From Figs. 9-12, a significant effect of leaching frequency on $COOH^*$ values is only observed for RS litter at 24 °C. For these conditions, the $COOH^*$ values of litter leachate organic acids are greatest in less frequently leached samples (the 4-day results are inconsistent with this generalization).

Intensity of Leaching Events

The effect of leaching intensity on litter leachate solution composition was evaluated by comparing the results obtained under standard conditions (1.0 cm/hr) with results obtained at leaching intensities of 0.25, 0.50, 2.0, and 4.0 cm/hr (see Figs. 17-18). Both cumulative WeakACY and TOC values are greater for RS litter samples than for NH samples; however, $COOH^*$ values are about the same for both litter types. For the most part, all leaching intensity experiments for both litter types fall within the standard conditions "windows", indicating that leaching intensity has no significant effect on cumulative WeakACY or cumulative TOC. Even within the leaching intensity experiments for a single litter type, there is no apparent effect of leaching intensity.

Fig. 17

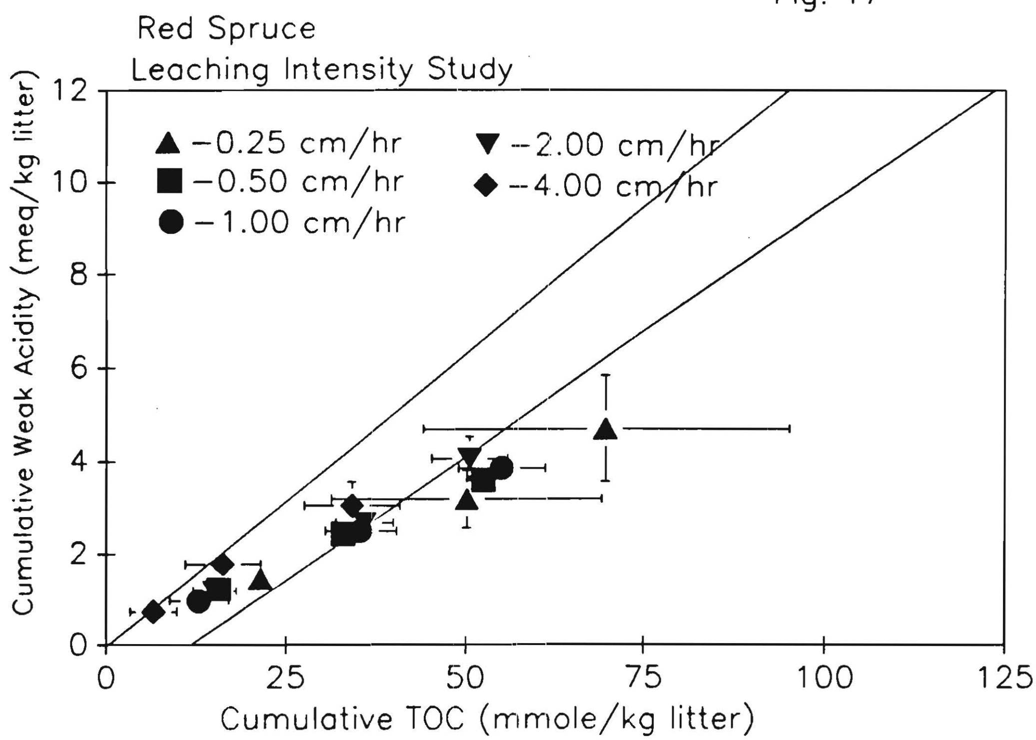
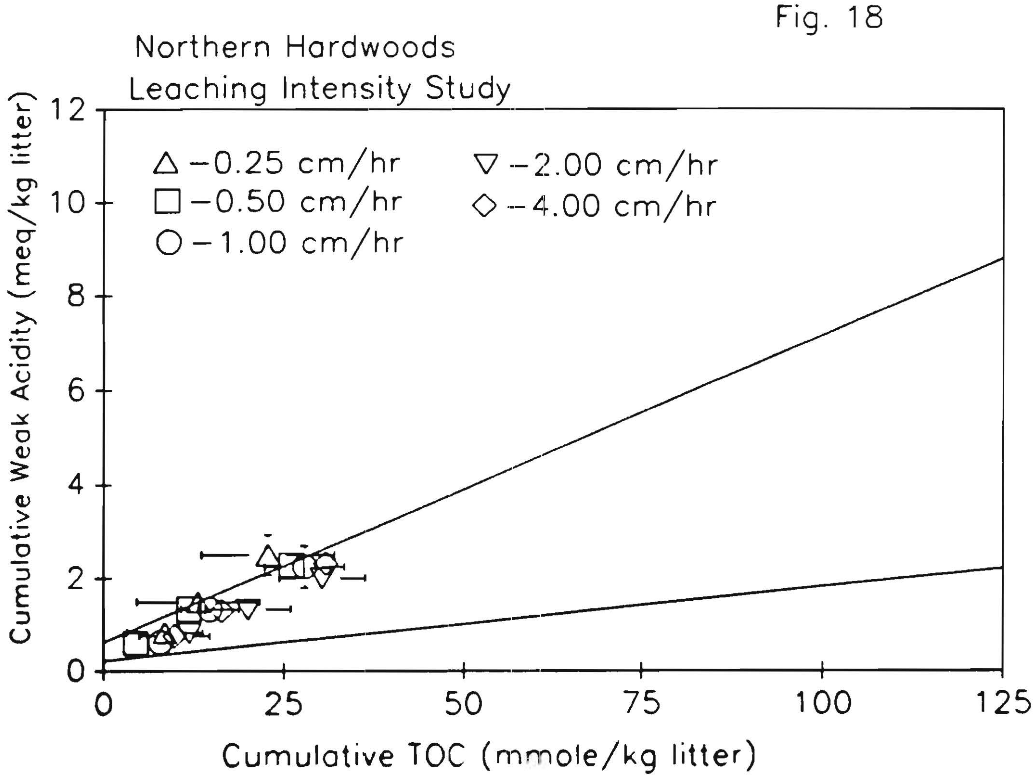

Red Spruce
Leaching Intensity Study
▲ −0.25 cm/hr
■ −0.50 cm/hr
● −1.00 cm/hr
▼ −2.00 cm/hr
◆ −4.00 cm/hr
Cumulative Weak Acidity (meq/kg litter)
0
2
4
6
8
10
12
0
25
50
75
100
125
Cumulative TOC (mmole/kg litter)

Fig. 18


Northern Hardwoods
Leaching Intensity Study
△ −0.25 cm/hr
□ −0.50 cm/hr
○ −1.00 cm/hr
▽ −2.00 cm/hr
◇ −4.00 cm/hr
Cumulative Weak Acidity (meq/kg litter)
0
2
4
6
8
10
12
0
25
50
75
100
125
Cumulative TOC (mmole/kg litter)

These experiments indicate that the rate of mobilization of organic matter from forest litter is sufficiently rapid that leaching intensity does not affect the flux of organic matter from forest litter into soil solutions. However, the actual flux of organic matter from a forest soil into surface waters is believed to be strongly dependent on hydrologic flow path. Conditions that (1) minimize contact time between percolating solutions and soil minerals and biota and (2) cause displacement of organic-rich waters into stream channels (e.g., from riparian zones) are particularly favorable for organic matter transport into surface waters.

Summary of Litter Leaching Experiments

This study was designed to estimate the magnitude of variation in WeakACY and TOC that might arise in a real forest watershed by studying the effects of litter type, temperature, pH of "rain", moisture of litter, frequency and intensity of leaching events on litter leachate solution chemistry. Prior discussion has indicated that some of the experimental parameters have a more profound effect than others. To better understand the general sensitivity of litter leachate composition to experimental leaching parameters, pertinent averages and standard deviations are given in Table 10. The WeakACY and TOC values in Table 10 (as well as the calculated parameter $COOH^*$) represent simple averages of net data over the course of each leaching experiment. Because WeakACY and TOC vary considerably over the course of a leaching experiment (generally decreasing each time a litter sample is leached), the standard deviations are rather large. It should be emphasized that these "standard deviations" arise from the changes in litter leachate composition that occur with successive leachings and not from experimental uncertainties in WeakACY and TOC values.

The results in Table 10 are grouped by major experiment. A comparison of results from RS and NH litter samples reveals that leachate solutions from RS litter contained higher WeakACY (except for the dry leaching experiment) and slightly higher TOC (except for the 24 °C leaching frequency study). The most dramatic effect on litter leach-

TABLE 10. Average WeakACY and TOC (μeq/kg litter) and COOH* Values (μeq/mg C) for Litter Leaching Experiments

	Red Spruce Litter			Northern Hardwoods Litter		
Experiment	WeakACY	TOC	COOH*	WeakACY	TOC	COOH*
2-day at 24°C[a]	666 ± 637	6.7 ± 4.5	7.7 ± 3.2	212 ± 87	7.8 ± 2.5	2.4 ± 1.2
4-day at 24°C[a]	825 ± 972	9.6 ± 10.3	6.8 ± 3.0	381 ± 193	10.9 ± 2.7	3.0 ± 1.5
8-day at 24°C[a]	1693 ± 1929	12.9 ± 9.3	9.0 ± 4.6	393 ± 203	15.6 ± 5.1	2.0 ± 0.7
16-day at 24°C[a]	2787 ± 2049	9.0 ± 4.4	25.0 ± 14.1	614 ± 280	20.8 ± 3.3	2.4 ± 0.9
2-day at 3°C[a]	437 ± 231	5.4 ± 2.3	7.6 ± 4.9	133 ± 90	4.8 ± 2.4	2.4 ± 1.6
4-day at 3°C[a]	512 ± 114	7.4 ± 2.9	6.7 ± 2.8	399 ± 298	6.9 ± 2.1	4.5 ± 2.6
8-day at 3°C[a]	682 ± 197	9.8 ± 3.2	6.5 ± 3.3	266 ± 86	7.2 ± 1.3	3.1 ± 1.2
16-day at 3°C[a]	780 ± 132	14.3 ± 3.9	4.7 ± 0.9	489 ± 131	7.1 ± 1.6	5.8 ± 1.3
pH 5.6 "Rain"[b]	533 ± 521	21.8 ± 9.8	1.8 ± 1.0	939 ± 436	12.3 ± 4.0	6.2 ± 1.4
pH 4.0 "Rain"[b]	1419 ± 1119	45.3 ± 20.6	2.4 ± 1.1	831 ± 334	12.7 ± 5.0	5.5 ± 1.2
pH 3.5 "Rain"[b]	1218 ± 988	40.8 ± 22.1	2.4 ± 0.8	924 ± 402	11.9 ± 3.3	6.4 ± 1.5
Wet Storage[c]	1215 ± 358	11.3 ± 4.8	12.8 ± 15.5	398 ± 242	8.6 ± 8.8	4.8 ± 2.6
Dry Storage[c]	1297 ± 605	22.5 ± 11.5	5.4 ± 2.2	2389 ± 1189	15.5 ± 8.0	13.4 ± 6.0
0.25 cm/hr[d]	1589 ± 481	23.2 ± 11.9	6.1 ± 0.9	857 ± 212	7.6 ± 3.9	11.1 ± 4.2
0.50 cm/hr[d]	1193 ± 150	16.5 ± 3.8	6.3 ± 1.5	785 ± 169	8.7 ± 4.7	9.4 ± 4.5
1.00 cm/hr[d]	1308 ± 280	18.4 ± 4.8	6.0 ± 0.5	772 ± 194	9.3 ± 3.4	7.3 ± 1.6
2.00 cm/hr[d]	1378 ± 248	16.9 ± 4.5	7.1 ± 1.4	692 ± 157	10.1 ± 3.3	6.6 ± 3.3
4.00 cm/hr[d]	1038 ± 285	11.4 ± 5.5	8.5 ± 2.4	799 ± 221	10.3 ± 4.5	7.7 ± 3.8

[a]Frequency/Temperature Study; [b]pH Study; [c]Moisture Study; [d]Intensity Study

ate composition was observed when litter samples were stored under dry conditions between leachings. For both RS and NH litters, TOC yields increased 100 percent, and the WeakACY of the NH litter leachate solution increased by 600 percent. Accordingly, $COOH^*$ was greater for NH and lower for RS under dry storage conditions. Lower leaching frequencies yield higher WeakACY and TOC values in almost all cases, consistent with the hypothesis that there is an accumulation of water-soluble organic matter between leaching events. The calculated $COOH^*$ values also appear to be generally greater in less frequently leached litter samples, suggesting that qualitative as well as quantitative changes are taking place in the accumulating water-soluble organic matter. There is a small, though perhaps insignificant, decrease in both WeakACY and TOC at lower temperature for both litter types at all leaching frequencies. This result is expected for biologically mediated litter degradation processes. Leaching intensity simply has no detectable effect on litter leachate solution chemistry, perhaps indicating that little or no production of water-soluble organic matter occurred during the contact time between litter and leaching solution (1.25-20.0 hr per leaching event).

Perhaps most surprising of all is the observation that the pH of leaching solutions has no effect on either WeakACY or TOC for both litter types. There is much current debate about the interaction between the strong mineral acids in rainfall and the organic acids in forest soils, with the general premise being that low pH rainfall mobilizes less organic acids than higher pH rainfall. This hypothesis appears to be derived from the observation that some fraction of litter leachate organic acids is insoluble in extremely acidic solutions. Under the conditions used in this study (pH 3.5, 4.0, or 5.6), this hypothesis appears to be invalid. As previously stated, the possibility remains that the pH of rainfall may otherwise affect organic acid transport through soil mineral horizons.

Isolation and Characterization of Leachate Organic Acids

The yields of extracted organic carbon (Table 4) in bulk litter leachate solutions vary greatly with both leaching conditions and litter type. The TOC concentrations of samples leached early in the study (Red Spruce pH 5.6 and 4.0 experiments) were much greater than those of samples leached later in the study, suggesting time-dependent changes in litter quality that hamper the interpretation of these data. If samples leached early in the study (RS pH 5.6 and 4.0) are excluded from the averaging process, the yields of extracted organic carbon are comparable for both litter types under identical leaching conditions.

Isolation and Preparation

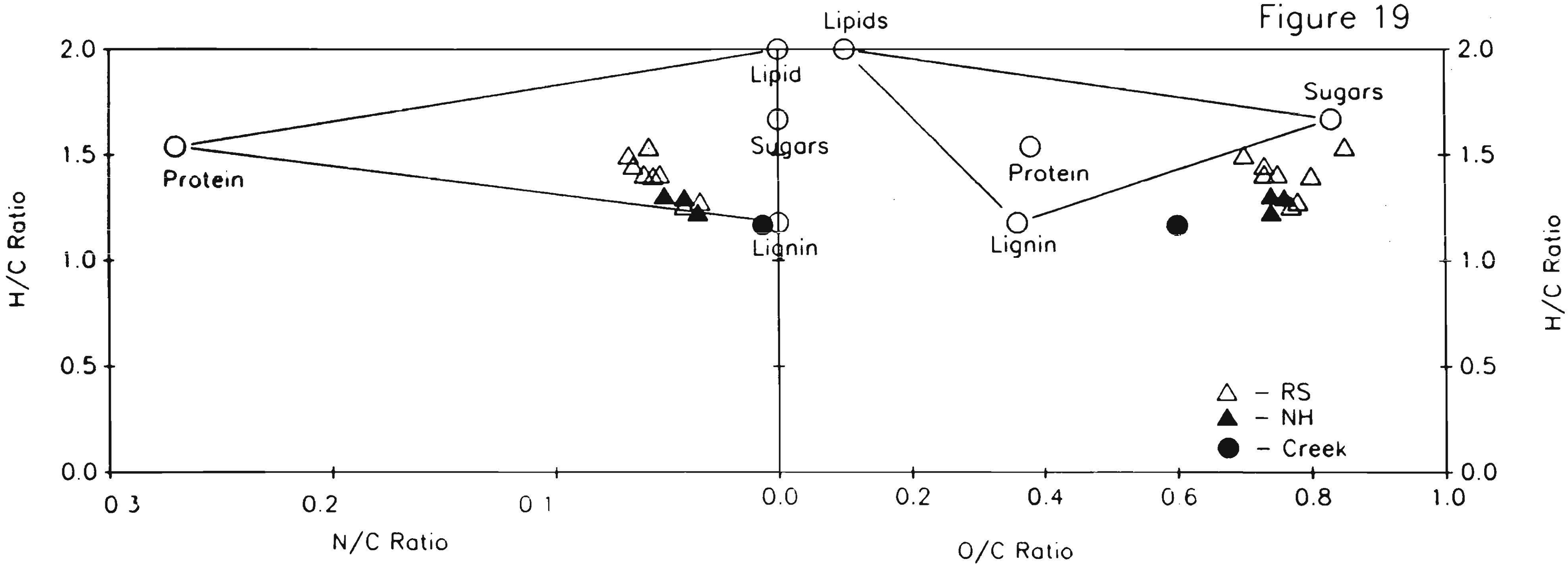
Isolation of litter leachate organic acids was completed via the experimental protocol outlined in the **EXPERIMENTAL** section of this report. The percentage carbon recoveries and organic carbon yields for all of the bulk leaching samples (Table 4) show great variability between experiments. There is a potentially significant greater average recovery for RS litter leachate organic matter (76%) than for NH litter leachate organic matter (57%), possibly indicating a greater abundance of low molecular weight components in the latter. Such small compounds are more likely to be lost in the ultrafiltration step.

Elemental analysis data are given in Table 6 for all isolated leachate samples and for the Raven Fork Creek sample. For a given litter type, the elemental analysis data are essentially independent of leaching parameters that were investigated in this study. There may be a slight difference in compositions of RS and NH samples, for which average H/C and N/C values differ to some extent (RS: H/C = 1.41 ± 0.10, N/C = 0.054 ± 0.011; NH: H/C = 1.28 ± 0.04, N/C = 0.043 ± 0.008). Both litter leachate sample types are different from the stream sample, for which H/C = 1.17 and N/C = 0.007. Additionally, the O/C ratio for the stream sample (0.60) is much lower than the average values for RS and NH litter leachate samples (0.75 ± 0.01 and 0.76 ± 0.05, respectively).

To place these elemental data in perspective, a van Krevelen plot is given in Figure 19, showing the atomic H/C, O/C, and N/C ratios not only for the samples in this study but also for the dominant biochemical precursors of these samples. In the H/C

Van Krevelen Plot of Elemental Data

Figure 19



versus O/C portion of this graph, all our organic acid samples lie outside the "biological triangle" that is defined by the compositions of lipids, lignin, and sugars. Their compositions therefore cannot be accounted for by any mixture of biomolecules or even the selective removal of more reactive biomolecules. Rather, significant alteration to non-biological molecules must have occurred in the litter leachate samples and especially in the stream sample. This alteration is most likely due to oxidation under either aerobic or fermentative conditions.

In the H/C versus N/C portion of Figure 19, all the litter leachate organic acids plot within the "biological triangle". The samples do, however, show large relative losses of nitrogen. Assuming that all organic nitrogen in our samples originated in proteins (N/C = 0.27), the maximum percentage of carbon in the form of residual protein in the litter leachate samples is 13-25%. The stream sample, however, could contain a maximum of only 3% of its carbon in the form of residual proteins. The relatively small efflux of nitrogen from the watershed is indicative of the selective degradation and/or adsorption of proteins during transport of litter leachate solutions through soil mineral horizons and into streams (Melillo and Eber, 1982; Berg and Ekbohm, 1983; McClaugherty et al., 1985).

The locus of litter leachate sample points for H/C versus O/C is close to the "sugars" end of the "lignin-sugars" line in Figure 19, making it reasonable to assume that the samples still contain significant amounts of both biopolymers, especially sugars. Accordingly, the samples should contain mostly aliphatic carbon, with aromatic carbon contents being limited to about 15-18% for the average litter leachate sample. Perdue (1984) developed a computational method that can estimate the most probable percent aromatic carbon for a complex mixture from its elemental composition and COOH content. Using the average elemental analysis data for litter leachate samples in Table 6 and the average COOH content of 4.87 meq/gC from Table 8, the most probable average aromatic carbon content of the litter leachate samples was calculated to be 20.3%. The composition of the stream sample is clearly closer to the composition of lignin than the compositions of the litter leachate samples, and appears to contain 30-40% aromatic carbon. The calculation procedure yields a most probable aromatic carbon content of 27.0% for this sample.

Functional Group Analysis

It was unfortunately not possible to isolate sufficient quantities of purified litter leachate organic acids for many samples, especially from NH leachate solutions. Most of those samples were contaminated with HCl that had been introduced during the ultrafiltration phase of sample isolation. Efforts to correct raw titration data for the presence of strong acids and/or bases in the isolated product were largely unsuccessful. A complete titration data set is available for the Red Spruce litter. These data are not contaminated with hydrochloric acid and will be used to investigate the effect of pH of synthetic rain, leaching frequency, storage temperature and moisture content on the acid-base properties of the resulting leachate organic acids. In poorly buffered natural waters that are susceptible to acidification, the ability of organic acids to affect pH or acid neutralizing capacity is related to their acidic strengths. Very weak acids such as phenols, enols, alcohols, etc. are not important contributors to surface water acidity because they cannot dissociate in the pH range of natural waters (pH 4-8). On the other hand, COOH groups, especially the more acidic ones, are likely to affect the acid-base chemistry of natural waters.

The titration curves of the isolated leachate organic acids, in the form of organic anion ($\Sigma[A_i^-]$) versus pH, are presented in Figures 20-21 (RS and NH, respectively). If the COOH content of a sample is assumed to be the $\Sigma[A_i^-]$ at pH 8.0, then the average COOH content of the leaf leachate organic acids is 5.05 ± 1.51 meq/g C with a range of 3.70 to 7.91 meq/g C over the entire range of leaching parameters and litter types that were investigated. Further, a qualitative visual inspection indicates that trends in $\Sigma[A_i^-]$ with pH are very similar for all leachate samples, suggesting similar underlying pK_a distributions of acidic functional groups. These results, all of which are model independent, were expected from the small scale leaching study and elemental analysis data.

Figure 20

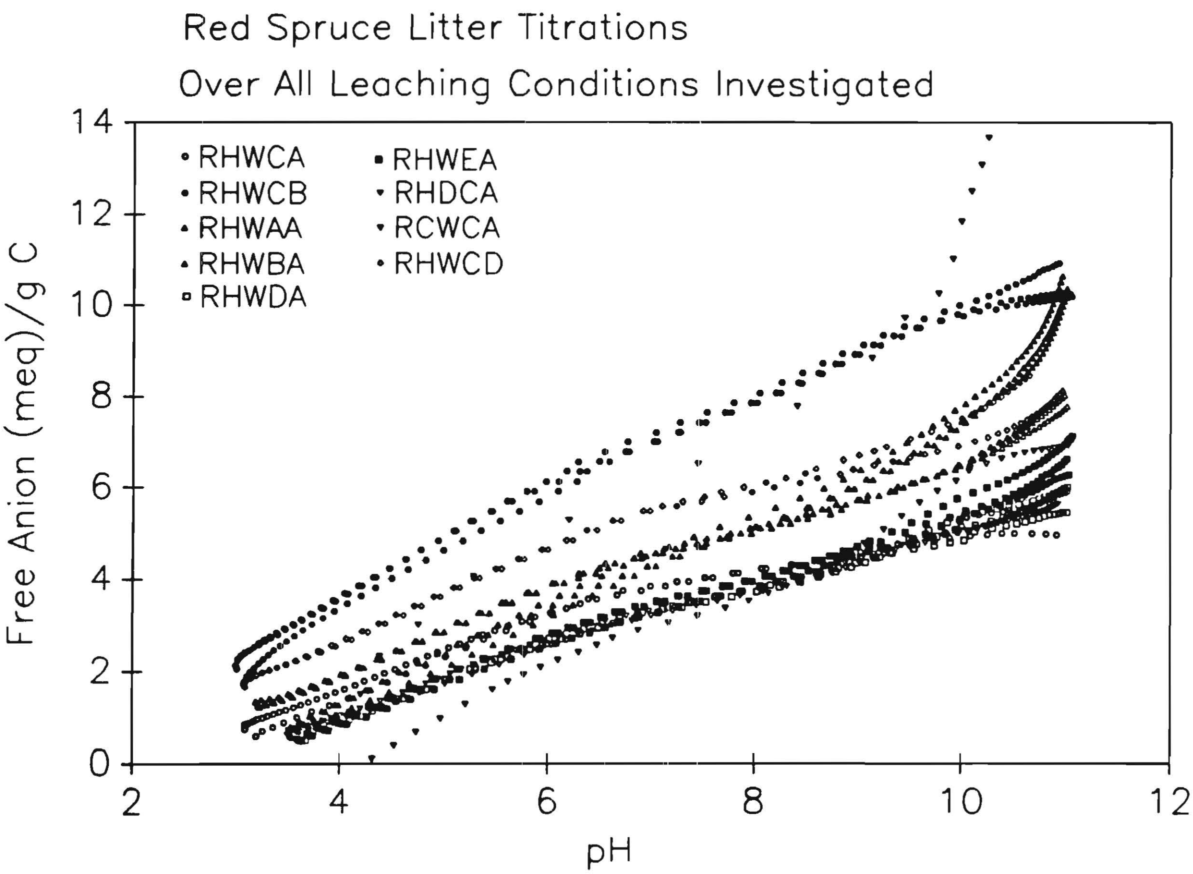
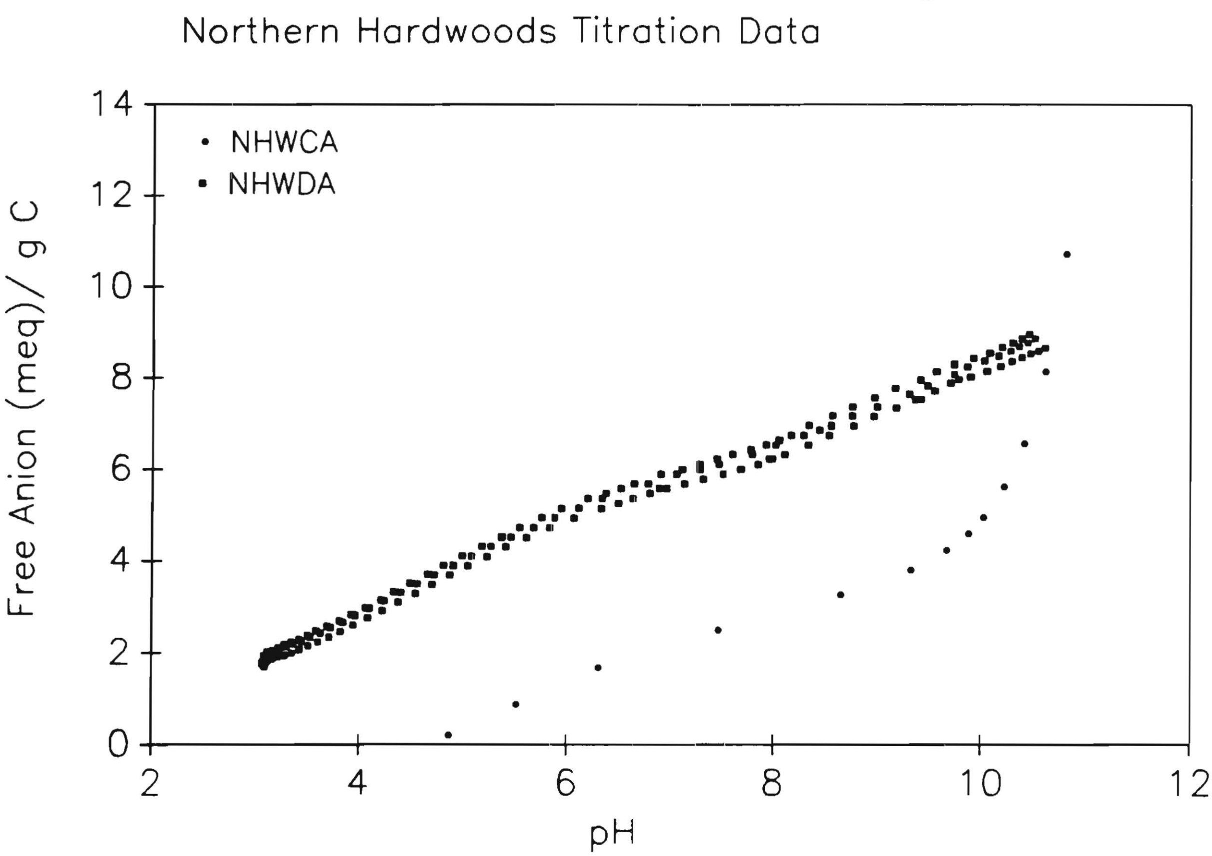

Red Spruce Litter Titrations
Over All Leaching Conditions Investigated
RHWCA
RHWCB
RHWAA
RHWBA
RHWDA
RHWEA
RHDCA
RCWCA
RHWCD
Free Anion (meq)/g C
pH
0
2
4
6
8
10
12
14
2
4
6
8
10
12

Figure 21

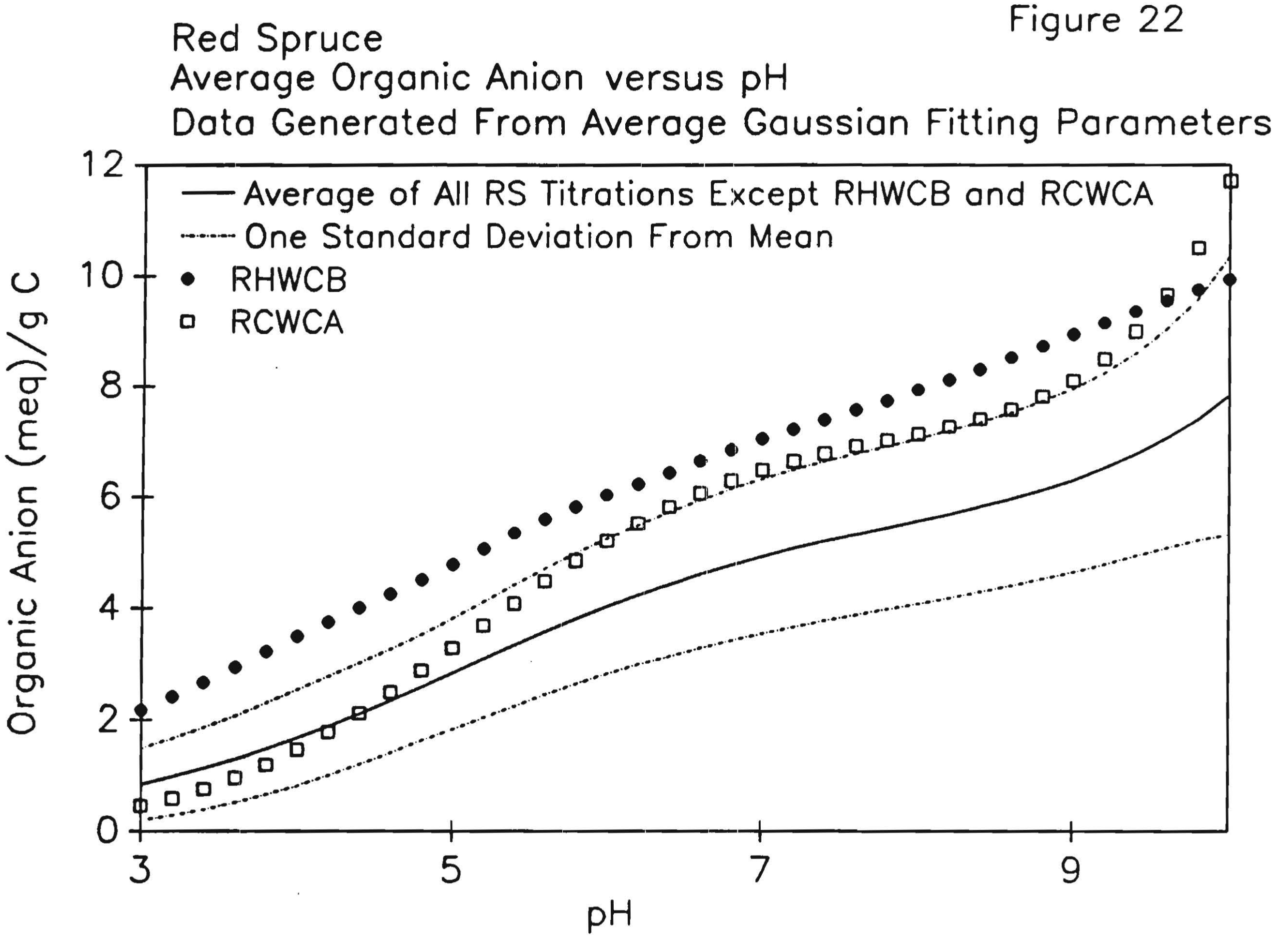

Northern Hardwoods Titration Data
NHWCA
NHWDA
Free Anion (meq)/ g C
pH
0
2
4
6
8
10
12
14
2
4
6
8
10
12

Given that (1) only the more acidic functional groups have a significant effect on acid-base chemistry and (2) the most accurate titration data are collected in the pH 3-9 range, mathematical models of the acid-base chemistry of the "strong" organic acids are sufficient to predict the contribution of organic acids to surface water acidification. Carboxyl contents were estimated as the observed $\Sigma[A_i^-]$ at pH 8.0, and the remaining fitting parameters of the bimodal Gaussian distribution model were determined by fitting the model to titration data (see Table 8). The average model fitting parameters for the samples listed in Table 4 for the first, "strong", acid sites are Conc = 5.05 ± 1.51 meq/gC, μ = 4.87 ± 0.38 and σ = 1.62 ± 0.36. These fitting parameters indicate that the mean COOH group has a pK_a that is close to the pK_a of acetic acid, but there are many stronger and weaker acids. In fact, 16% of the COOH groups have pK_a values that are less than 3.25. The relatively small standard deviations obtained for these fitting parameters indicate that the acid-base chemistry of isolated leachate organic acids was relatively insensitive to the litter leaching conditions that were used.

To facilitate comparisons of individual experiments with the average behavior of the litter leachate samples, a composite "average" titration curve was constructed. Using the model fitting parameters for each sample (Table 8), simulated titration data were generated over the pH 3-11 range at 0.2 pH intervals. At each pH, the mean and standard deviations of $\Sigma[A_i^-]$ were calculated. The average titration curve and its one-standard-deviation range are presented in Figure 22. While most of the samples were leached at 24 °C with pH 5.6 synthetic rain, the RHWCB sample was leached with pH 4.0 synthetic rain and the RCWCA sample was stored at 3 °C prior to leaching. Both the titration curves (Figure 20) and model fitting parameters (Table 8) of the RHWCB and RCWCA samples indicate that they may differ substantially from other samples, so their generated titration curves are superimposed on the average titration curve in Figure 22.

The titration curve of the RHWCB sample shows roughly the same trends in $\Sigma[A_i^-]$ with pH as the average titration curve, but $\Sigma[A_i^-]$ is higher at all pH values by an approximately constant amount. Although we have no ancillary data that can explain this obser-

Figure 22


Red Spruce
Average Organic Anion versus pH
Data Generated From Average Gaussian Fitting Parameters
Average of All RS Titrations Except RHWCB and RCWCA
One Standard Deviation From Mean
RHWCB
RCWCA
Organic Anion (meq)/g C
pH
0
2
4
6
8
10
12
3
5
7
9

vation, the vertical shift in the titration curve is consistent with the presence of a small amount of a strongly acidic contaminant in the sample. Alternatively, it is possible that low pH leaching solutions selectively mobilize organic acids with higher carboxyl contents, although pK_a values seem to be independent of the pH of the leaching solution.

Titration data from the RCWCA sample stored at 3 °C prior to leaching are suspect for the following reasons: (1) only enough material was isolated to perform one titration and (2) the titration was conducted at a relatively low TOC concentration (41.6 mg C/L). In the single titration curve for this sample (see Figure 22), $\Sigma[A_i^-]$ was unusually low at low pH and was extremely high at high pH. These potential errors in $\Sigma[A_i^-]$ are consistent with small errors in measured pH values (0.01-0.05 pH) over the course of the titration. The effect of pH measurement errors on $\Sigma[A_i^-]$ is greatest at very low and very high pH values, and is relatively larger at low DOC concentration (Perdue, 1990).

Whether the low pH of the leaching solution and lower storage temperature are responsible for the somewhat high carboxyl contents of these samples is unknown. Even if these are real effects rather than experimental artifacts, the carboxyl contents of leachate samples still lie within a narrow range of 3.7-7.9 meq/gC under all leaching conditions. These values agree well with other estimates for litter-derived organic acids (Schnitzer, 1959; Cronan and Aiken, 1985).

Although we were unable to isolate sufficient quantities of clean NH leachate samples to complete a full characterization of this litter type, enough uncontaminated leachate organic matter was isolated for two NH leachate samples (Figure 21) to provide a basis for comparison with RS litter leachates. From these limited data for NH litter, the organic acid leachate chemistry appears to be largely insensitive to litter type. The average data for each litter type from Table 8, for those samples meeting the 4d test, show that the average of all Gaussian distribution fitting parameters for NH, except μ for the second set of sites, lie within one standard deviation of the average fitting parameters for RS.

Data from both elemental analysis and acid-base titration of the Raven Fork Creek sample indicate that the organic matter in the surface water associated with the watershed where the litter samples were collected is significantly different from the forest litter leachate organic matter. Titration curves of the Raven Fork Creek sample (Figure 23) show a very different shape, somewhat flatter, than the titration curves for the litter leachate organic matter. Differences in these titration curves leads to a much lower COOH content (3.6 ± 0.2 meq/g C) in the creek sample than that observed for the average litter leachate organic matter (5.05 ± 1.51 meq/g C). Further, the COOH content of the creek sample is much lower than the commonly assumed estimate of 10 meq/g C for aquatic humic substances (Oliver et al., 1983), perhaps because the acid-base properties of humic substances do not adequately describe the acid-base properties of unfractionated DOC samples.

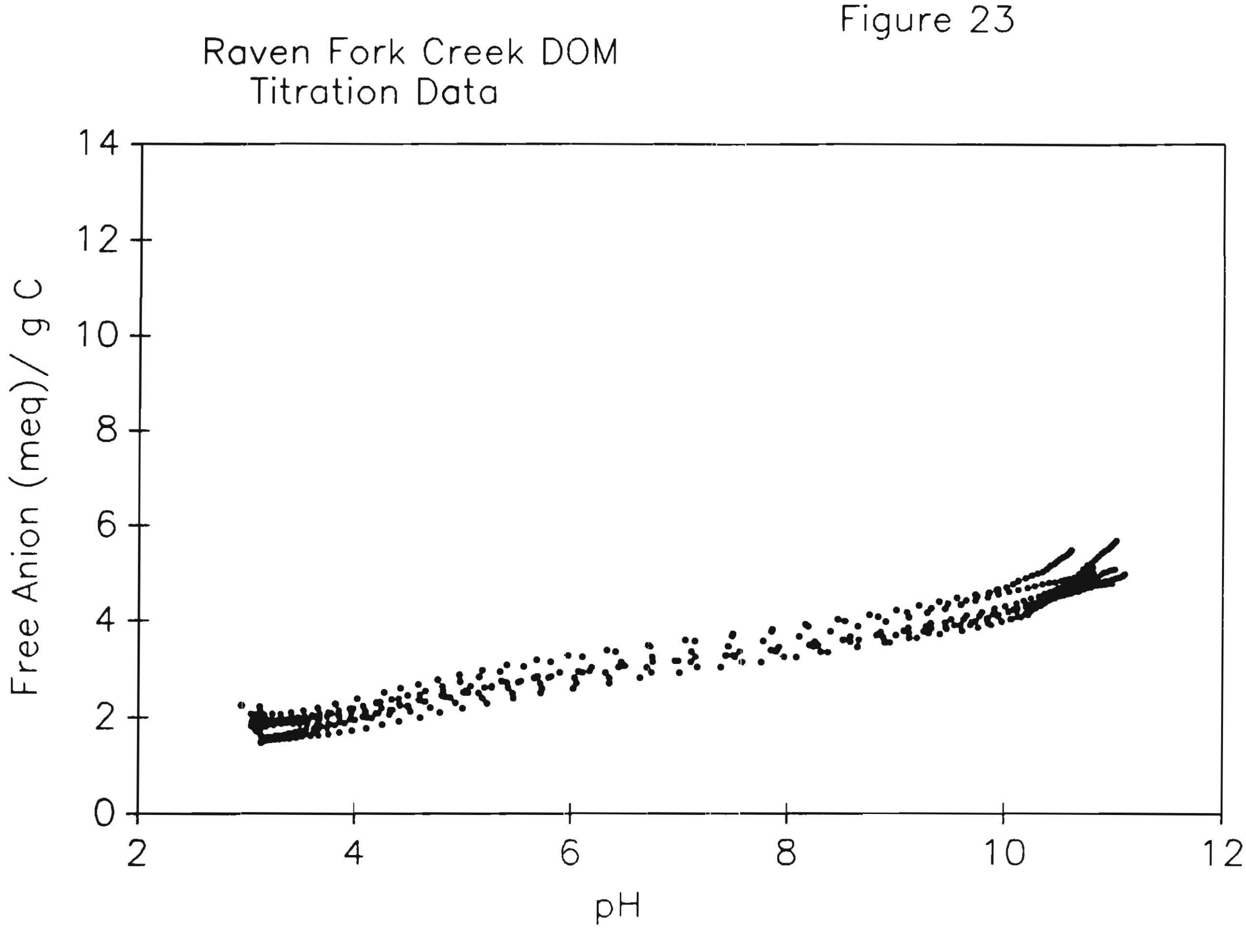
Modeling Gran Titration Estimates of Strong and Weak Acidity

The preceding discussion supports the existence of a broad distribution of acidic functional groups in litter leachate organic acids. When such mixtures of acids are reacted with strong acid in an alkalinity titration or with strong base in an acidity titration, significant reaction occurs over a very wide pH range. Distinct titration equivalence points are not observed. Nevertheless, Gran plots of titration data do produce x-axis intercepts that are commonly interpreted as strong acidity and total acidity in acidity titrations.

It is evident in Table 9 that about 30% of the carboxyl groups in litter leachate organic acids are so strongly acidic that they are labeled as "strong" acids according to Gran terminology. The remaining 70% of the carboxyl groups and all other acidic functional groups (e.g., phenols) are protonated at the Gran strong acidity titration endpoint. Assuming that all the carboxyl groups are reacted at the total acidity titration endpoint, the Gran total acidity measurement detects only about 46% of the phenols and other weak acids. It can be concluded that Gran plots cannot quantify either carboxyl or phenolic groups in litter leachate organic acids.

Although the results in Table 9 are presented from the perspective of an acidity titration, they are equally valid for alkalinity titrations. The Gran strong acidity endpoint

Figure 23


Raven Fork Creek DOM
Titration Data
Free Anion (meq)/ g C
14
12
10
8
6
4
2
0
2
4
6
8
10
12
pH

is the same as the Gran alkalinity endpoint that is detected when excess strong acid is added to a water sample. Accordingly, up to 70% of the carboxyl groups in litter leachate organic acids can be protonated during alkalinity titrations, possibly being interpreted as HCO_3^-. The remaining 30% of carboxyl groups are not detected and are classified as "strong" acid anions.

To place the contributions of organic acid anions in quantitative perspective, consider their contribution to the acid-base chemistry of a water sample containing 100 μeq/L of HCO_3^- and a DOC concentration of 8 mg/L. Depending on the initial pH of the sample, a Gran alkalinity titration would detect the 100 μeq/L of HCO_3^- and up to 28.4 μeq/L of carboxyl groups. The remaining 12.0 μeq/L of carboxyl groups would not be detected. A more complete treatment of the effects of organic acids on Gran ANC titrations has been presented by Cantrell et al., 1990.

Conclusions and Interpretations

If all leaching parameters in the litter leaching experiments are considered, there are substantial variations in the measured WeakACY (746 ± 771 μeq/kg litter) and TOC (145.9 ± 143.6 mgC/kg litter) values of litter leachate solutions. Because these two parameters tend to co-vary, there is less variability in their ratio COOH* (5.9 ± 5.1 meq/gC). Both WeakACY and COOH* represent an upper boundary of organic acidity, so actual COOH values of isolated litter leachate organic acids (5.05 ± 1.51 meq/gC, see Table 8) are predictably somewhat smaller. A major conclusion of this study is that the leaching conditions covered by our experiments do not significantly affect the amount of acidity per gram of organic carbon in litter leachate organic matter.

Although the COOH content of litter leachate organic acids appears to be independent of litter type and litter storage and leaching conditions, these parameters do reportedly affect the actual export of DOC (and thus organic acidity). Cronan and Aiken (1985) reported that DOC export is about 20% greater during summer months. Coniferous forests typically export about 50% more carbon than hardwood forests (Cronan, 1990).

Krug and Isaacson (1984) found that extremely acidic leaching solutions (pH 3.0) mobilized less DOC than distilled water. In a given forested ecosystem, DOC concentrations vary as precipitation (1-3 mgC/l) passes through the forest canopy (8-12 mgC/l), into soil litter horizons (15-50 mgC/l), into deeper soil mineral horizons, e.g. the B-horizon (4-8 mgC/l), and finally into groundwater (1-3 mgC/l). Depending on watershed hydrogeology and antecedent conditions, various hydrologic pathways can become active during recharge of surface waters. This natural variation in hydrologic flow path gives rise to variations in the export of DOC and organic acidity. There appears to be an inverse relationship between DOC and water flow, and DOC values are generally higher in areas that are not well drained (McDowell and Likens, 1988). The DOC variations that have been reported in these field studies are the integrated result of many of the leaching parameters that were investigated in this study.

Some of the leaching parameters in this study were varied in an attempt to emulate natural storage conditions of the litter **before** a leaching event (leaching frequency, temperature and moisture of litter during storage). Other leaching parameters were chosen to examine conditions **during** a leaching event (pH and intensity of synthetic rain). It appears that litter storage conditions have the greatest effect on mobilization of DOC and organic acidity. The leaching frequency study suggests that the DOC export per leaching event is greater in less frequently leached samples. This effect is greatly diminished when the litter is stored at 3 °C, with DOC export being generally lower than at 24 °C. Storage of litter under dry and presumably more oxidizing conditions causes the greatest increases in mobilization of DOC. The actual leaching conditions (pH of synthetic rain and leaching intensity) have little effect on either DOC or COOH. Slightly greater DOC export is found for RS than for NH litter, but the difference is much less than 50 percent (see Cronan, 1990).

Neither the concentration nor the acid-base properties of DOC mobilized from litter horizons can be used to accurately model the behavior of the organic matter that ultimately finds its way to surface waters under normal base flow conditions. The observed differences in the acid-base properties and elemental compositions of litter leachate organic acids and Raven Fork Creek DOM arise largely from alteration and fractionation of the organic matter as it moves through various hydrological pathways. During heavy precipitation events, where lateral flow from the forest litter horizons may be expected to dominate the hydrologic flow, the organic acids reaching surface waters would be expected to be more like litter leachate organic matter. Under low flow conditions, the organic matter from forest litter would be expected to migrate slowly through soil mineral horizons. The correspondingly longer residence time allows greater microbial alteration and respiration of biologically labile components of DOM. Some components of DOM may be chemically adsorbed in the deeper mineral soil horizons.

The Raven Fork Creek sample was isolated at a time of very low flow during the drought of the summer of 1986. The organic matter collected at this time should have come largely from the lower soil horizons. This sample contained slightly less carboxyl groups (4.48 meq/gC) than average litter leachate organic matter (5.05 meq/gC). However, the carboxyl groups of Raven Fork Creek DOM are much more acidic than those of litter leachate organic matter (μ values of 3.02 and 4.87, respectively). Elemental composition data indicate that the stream sample has undergone much more extensive alteration that resulted in carbon enrichment and nitrogen depletion relative to the litter leachate samples.

Predictive models of the flux of organic acidity from forest litter should be able to assume that the flux of organic acidity is proportional to the flux of DOC, given the relatively constant COOH content that was observed in this study. The flux of organic acidity from a forested watershed (meq/m^2) can thus be estimated as:

$$\text{Organic Acidity} = \text{DOC (mg C/l)} * \text{COOH } (\mu\text{eq/mg C}) * \text{R (m)} * (1 \text{ meq-l}/\mu\text{eq-m}^3)$$

where R is the meters of water that reach the surface water. Using DOC and COOH data from the litter leaching experiments and scaling the results for an annual rainfall of 1 m, the estimated fluxes of DOC and organic acidity from forest litter in the Raven Fork watershed are 77 g C/m^2-yr and 388 meq/m^2-yr, respectively. This DOC flux is much greater than the estimate of 2.15 g C/m^2-yr for the world average river (Maybeck, 1982) and the reported value of 3.6 g C/m^2-yr for a northeastern hardwood system (Cronan, 1990). Given these results and the low observed DOC value in Raven Fork Creek, we estimate that only 3-5 percent of initially mobilized DOC reaches the stream. Even so, the annual flux of organic acidity (12-20 meq/m^2-yr) is 90-150 percent of the annual flux of acidic deposition in the Raven Fork watershed (13 meq/m^2-yr, from 1 m/yr of pH 4.9 rain).

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APPENDICES

In Appendices A-C, each kind of leaching experiment has been assigned a code number. In Appendix A, the three replicates of a given type of experiment have the same code number. The explanation of these codes is given below. Codes 1-16 are assigned to the experiments on the effects of temperature and leaching frequency. Codes 17-22 are assigned to the study of the effects of the pH of the leaching solutions. Codes 23-26 are assigned to the study of the effects of moisture content of stored litter. Codes 27-36 are assigned to the experiments on the effects of leaching rate (cm/hr).

		Storage Conditions			Leaching Conditions	
Code	Litter Type	Temp °C	Moisture	Days	Rate (cm/hr)	pH
1	Red Spruce	24	Wet	2	1.00	5.6
2	Red Spruce	24	Wet	4	1.00	5.6
3	Red Spruce	24	Wet	8	1.00	5.6
4	Red Spruce	24	Wet	16	1.00	5.6
5	Red Spruce	3	Wet	2	1.00	5.6
6	Red Spruce	3	Wet	4	1.00	5.6
7	Red Spruce	3	Wet	8	1.00	5.6
8	Red Spruce	3	Wet	16	1.00	5.6
9	N. Hardwoods	24	Wet	2	1.00	5.6
10	N. Hardwoods	24	Wet	4	1.00	5.6
11	N. Hardwoods	24	Wet	8	1.00	5.6
12	N. Hardwoods	24	Wet	16	1.00	5.6
13	N. Hardwoods	3	Wet	2	1.00	5.6
14	N. Hardwoods	3	Wet	4	1.00	5.6
15	N. Hardwoods	3	Wet	8	1.00	5.6
16	N. Hardwoods	3	Wet	16	1.00	5.6
17	Red Spruce	24	Wet	2	1.00	5.6
18	Red Spruce	24	Wet	2	1.00	4.0
19	Red Spruce	24	Wet	2	1.00	3.5
20	N. Hardwoods	24	Wet	2	1.00	5.6
21	N. Hardwoods	24	Wet	2	1.00	4.0
22	N. Hardwoods	24	Wet	2	1.00	3.5
23	Red Spruce	24	Wet	2	1.00	5.6
24	Red Spruce	24	Dry	2	1.00	5.6
25	N. Hardwoods	24	Wet	2	1.00	5.6
26	N. Hardwoods	24	Dry	2	1.00	5.6
27	Red Spruce	24	Wet	2	0.25	5.6
28	Red Spruce	24	Wet	2	0.50	5.6
29	Red Spruce	24	Wet	2	1.00	5.6
30	Red Spruce	24	Wet	2	2.00	5.6
31	Red Spruce	24	Wet	2	4.00	5.6
32	N. Hardwoods	24	Wet	2	0.25	5.6
33	N. Hardwoods	24	Wet	2	0.50	5.6
34	N. Hardwoods	24	Wet	2	1.00	5.6
35	N. Hardwoods	24	Wet	2	2.00	5.6
36	N. Hardwoods	24	Wet	2	4.00	5.6

APPENDIX A. Raw Uncorrected Concentrations (μeq/l) of Major Solutes

CODE	DAY	Exp pH	H	K	NH4	Cl	NO3	SO4	TotACY	WeakACY	TOC(mM)
1	0	5.53	3.5	25	141	5	17	9	463	319	1.0
	2	5.21	7.3	73	352	8	43	15	1984	1625	9.8
	4	5.15	8.3	34	211	4	67	19	738	519	5.3
	6	5.29	6.0	43	240	4	121	27	1008	762	4.8
	8	5.25	6.6	21	167	3	141	24	675	501	4.3
	10	5.23	7.0	18	162	2	96	21	620	451	3.8
	12	5.29	6.0	22	156	2	91	14	567	405	2.7
	14	4.88	15.6	20	151	3	85	11	511	344	2.0
	16	4.86	16.1	14	111	4	139	15	428	301	3.8
	18	4.88	15.4	12	101	6	121	19	331	215	3.8
	20	4.87	16.0	10	87	5	84	15	400	297	2.3
	22	4.99	12.0	8	76	4	64	15	221	133	1.0
	24	5.03	11.1	6	58	2	49	11	156	87	2.7
	26	5.28	6.2	7	61	2	58	5	168	101	2.5
	28	4.92	14.3	5	60	2	36	4	201	127	1.3
	30	5.39	4.8	5	62	3	42	4	196	129	1.0
	32	5.35	5.2	3	56	3	45	5	185	124	1.1
1	0	5.47	4.0	18	100	4	16	10	441	337	1.0
	2	5.28	6.2	61	322	5	35	13	1658	1330	9.3
	4	5.24	6.8	33	191	3	66	16	775	577	6.6
	6	5.38	4.9	37	162	4	106	26	936	769	5.1
	8	5.21	7.2	19	97	3	123	19	657	553	5.2
	10	5.24	6.7	24	120	2	87	18	564	437	4.8
	12	5.34	5.4	18	88	2	79	13	521	428	3.6
	14	5.15	8.4	13	98	2	81	10	373	267	3.5
	16	4.73	22.0	10	92	3	142	17	300	186	3.0
	18	4.82	17.8	6	60	5	108	16	276	198	2.8
	20	4.75	21.0	6	65	4	96	18	320	234	2.7
	22	5.07	10.0	5	48	3	79	13	230	172	1.9
	24	5.24	6.7	4	46	1	48	7	128	75	2.0
	26	5.47	4.0	3	50	2	59	3	134	80	1.4
	28	5.07	10.0	3	44	2	32	3	150	96	1.5
	30	5.73	2.2	3	50	2	39	3	150	98	1.7
	32	5.36	5.1	3	33	3	42	6	150	112	1.6
1	0	5.39	4.8	20	110	3	14	11	353	238	1.0
	2	5.21	7.2	49	298	5	29	10	1542	1237	12.9
	4	5.28	6.2	44	162	3	61	15	716	548	6.3
	6	5.36	5.1	37	207	3	100	21	876	664	4.1
	8	5.29	6.0	29	144	2	99	16	590	440	4.8
	10	5.29	6.1	18	150	1	81	14	520	364	4.4
	12	5.39	4.8	14	122	2	65	11	478	351	3.1
	14	4.97	12.6	18	81	2	75	9	436	342	2.7
	16	4.82	18.0	12	97	2	118	12	322	207	2.6
	18	4.96	13.0	12	73	4	95	15	233	147	2.3
	20	4.92	14.0	8	73	3	94	13	270	183	2.2
	22	5.17	8.0	5	62	3	89	11	176	106	1.9
	24	5.11	9.2	5	52	3	42	9	139	78	2.7
	26	5.39	4.8	5	54	2	45	4	148	89	3.0
	28	5.00	11.7	4	55	2	36	5	189	122	2.9
	30	5.77	2.0	4	56	2	35	3	164	106	1.1
	32	5.47	4.0	3	37	2	47	4	160	119	2.2

APPENDIX A. Raw Uncorrected Concentrations (μeq/l) of Major Solutes

CODE	DAY	Exp pH	H	K	NH4	Cl	NO3	SO4	TotACY	WeakACY	TOC(mM)
2	0	5.53	3.5	25	141	5	17	9	463	319	1.0
	4	4.95	13.3	123	496	10	41	20	2020	1511	18.8
	8	4.85	16.7	52	260	8	72	25	763	486	5.8
	12	4.54	33.7	44	189	6	119	27	545	322	4.8
	16	4.59	30.0	25	95	6	126	26	279	154	2.6
	20	4.82	17.7	22	60	4	108	19	210	132	2.1
	24	4.87	15.9	18	59	4	75	17	230	155	1.8
	28	4.73	22.0	12	60	4	54	11	253	171	2.8
	32	4.62	28.0	9	73	3	65	11	274	173	1.5
2	0	5.47	4.0	18	100	4	16	10	441	337	1.0
	4	4.76	20.5	109	528	11	49	32	1988	1440	8.0
	8	4.81	18.1	44	374	7	94	29	1000	608	4.2
	12	4.49	38.1	25	225	6	146	33	654	391	2.5
	16	4.53	35.0	18	124	5	169	28	294	135	2.6
	20	4.77	20.0	15	79	3	149	22	238	139	1.8
	24	4.79	19.1	16	85	3	98	18	229	125	2.1
	28	4.65	26.2	7	88	3	56	14	240	126	1.7
	32	4.59	30.0	6	92	3	77	19	253	131	1.9
2	0	5.39	4.8	20	110	3	14	11	353	238	1.0
	4	4.87	15.7	92	563	7	47	21	2604	2025	23.5
	8	4.75	20.8	36	329	5	105	31	1108	758	10.4
	12	4.42	44.6	27	210	5	131	40	781	526	6.0
	16	4.43	43.3	20	108	4	146	32	327	176	3.7
	20	4.72	22.3	20	68	4	121	26	251	161	4.0
	24	4.64	27.0	14	72	2	99	20	276	177	3.6
	28	4.60	29.8	14	77	3	77	17	278	171	3.4
	32	4.53	35.0	9	78	3	84	22	346	233	2.2
3	0	5.53	3.5	25	141	5	17	9	463	319	1.0
	8	4.50	37.0	188	1014	12	129	30	3363	2312	13.6
	16	4.08	98.5	63	347	9	157	38	1015	570	5.7
	24	4.18	77.2	42	251	7	100	22	541	213	5.3
	32	4.16	81.2	56	278	7	118	23	561	202	1.8
3	0	5.47	4.0	18	100	4	16	10	441	337	1.0
	8	4.43	44.0	175	862	14	107	37	3824	2918	12.8
	16	4.17	80.2	57	344	10	141	49	1070	646	6.7
	24	4.33	55.0	36	217	8	89	39	588	316	2.8
	32	4.18	77.6	44	260	8	105	46	572	234	2.1
3	0	5.39	4.8	20	110	3	14	11	353	238	1.0
	8	4.55	33.0	165	797	12	97	32	3196	2366	16.5
	16	4.23	70.0	42	296	8	131	44	984	618	6.5
	24	4.39	47.8	30	210	5	83	28	461	203	5.1
	32	4.34	54.2	35	230	7	98	29	382	98	2.4
4	0	5.53	3.5	25	141	5	17	9	463	319	1.0
	16	4.22	70.7	212	1388	14	167	47	3396	1937	8.8
	32	3.99	121.0	218	936	15	254	53	1430	373	3.8

APPENDIX A. Raw Uncorrected Concentrations (μeq/l) of Major Solutes

CODE	DAY	Exp pH	H	K	NH4	Cl	NO3	SO4	TotACY	WeakACY	TOC(mM)
4	0	5.47	4.0	18	100	4	16	10	441	337	1.0
	16	4.33	55.6	188	1502	19	156	67	3690	2132	4.4
	32	4.26	64.0	184	1019	26	222	81	1567	484	2.7
4	0	5.39	4.8	20	110	3	14	11	353	238	1.0
	16	4.43	43.8	314	1568	18	139	54	4677	3065	5.9
	32	4.29	60.0	231	1006	18	199	61	1875	809	2.7
5	0	5.53	3.5	25	141	5	17	9	463	319	1.0
	2	5.67	2.5	43	153	11	25	16	540	385	2.1
	4	5.89	1.5	25	125	15	40	20	345	219	5.8
	6	6.23	0.7	11	80	5	24	17	262	181	2.7
	8	6.47	0.4	10	67	2	21	10	195	128	1.9
	10	5.99	1.2	7	71	2	22	10	278	206	2.4
	12	6.59	0.3	8	107	2	33	11	235	128	1.8
	14	6.77	0.2	6	91	3	14	7	200	109	2.4
	16	5.87	1.6	12	144	5	7	12	315	169	1.7
	18	6.59	0.3	4	109	4	39	13	211	102	2.3
	20	6.23	0.7	6	114	3	44	8	218	103	1.0
	22	6.47	0.4	7	110	2	40	8	221	111	1.0
	24	6.29	0.6	6	98	4	61	5	226	127	2.8
	26	6.77	0.2	5	75	2	27	6	188	113	3.6
	28	6.29	0.6	4	67	2	15	5	231	163	2.4
	30	6.23	0.7	5	91	2	16	5	227	135	1.6
	32	6.29	0.6	4	74	2	19	6	230	155	1.3
5	0	5.47	4.0	18	100	4	16	10	441	337	1.0
	2	5.61	2.9	67	244	9	22	14	1020	773	1.9
	4	5.87	1.6	50	198	13	34	23	560	360	5.3
	6	6.03	1.1	26	139	5	32	21	471	331	2.6
	8	6.37	0.5	20	109	3	26	18	355	246	2.8
	10	5.82	1.8	17	129	2	18	13	425	294	2.9
	12	6.47	0.4	15	75	2	37	6	378	303	4.0
	14	6.77	0.2	10	60	3	16	4	245	185	2.4
	16	5.82	1.8	16	112	5	20	7	400	286	2.4
	18	6.77	0.2	7	59	4	54	9	228	169	3.7
	20	6.37	0.5	6	65	2	28	6	248	183	2.2
	22	6.37	0.5	5	50	2	38	5	244	194	2.1
	24	6.37	0.5	6	54	3	58	5	253	199	2.1
	26	6.59	0.3	6	52	2	19	5	235	183	2.2
	28	6.03	1.1	4	52	2	12	5	255	202	1.6
	30	6.23	0.7	6	62	2	12	4	261	198	1.9
	32	6.37	0.5	3	58	2	17	5	281	223	1.8
5	0	5.39	4.8	20	110	3	14	11	353	238	1.0
	2	5.64	2.7	58	188	6	16	12	810	619	2.9
	4	6.17	0.8	42	145	10	27	17	475	329	6.6
	6	6.12	0.9	17	105	4	20	24	368	262	4.0
	8	6.47	0.4	15	88	2	19	21	230	142	3.1
	10	5.89	1.5	15	94	2	15	15	338	243	3.9
	12	6.77	0.2	10	85	1	11	10	305	220	2.5
	14	6.77	0.2	11	74	1	13	6	275	201	3.7
	16	6.17	0.8	20	131	3	4	11	475	343	3.4

APPENDIX A. Raw Uncorrected Concentrations (μeq/l) of Major Solutes

CODE	DAY	Exp pH	H	K	NH4	Cl	NO3	SO4	TotACY	WeakACY	TOC(mM)
5	18	6.77	0.2	10	75	3	31	17	311	236	5.0
	20	6.23	0.7	9	85	2	22	10	323	237	2.3
	22	6.37	0.5	7	89	2	32	8	330	241	3.4
	24	6.37	0.5	6	82	2	45	7	322	240	4.4
	26	6.59	0.3	4	68	2	14	3	297	229	3.6
	28	6.07	1.0	5	55	1	9	3	312	256	3.6
	30	6.47	0.4	5	72	1	10	3	253	181	1.7
	32	6.37	0.5	3	69	1	15	4	266	197	2.6
6	0	5.53	3.5	25	141	5	17	9	463	319	1.0
	4	5.99	1.2	67	116	6	29	22	475	358	2.5
	8	6.17	0.8	44	109	7	36	19	378	268	2.8
	12	6.17	0.8	58	107	6	34	15	350	242	3.1
	16	5.33	5.5	78	175	3	38	17	580	400	3.6
	20	6.23	0.7	54	130	3	31	15	505	374	3.7
	24	5.73	2.2	43	111	3	27	8	430	317	5.6
	28	5.75	2.1	39	125	2	21	6	450	323	4.2
	32	5.77	2.0	45	110	3	24	7	415	303	2.2
6	0	5.47	4.0	18	100	4	16	10	441	337	1.0
	4	6.12	0.9	29	101	9	35	32	392	290	2.5
	8	6.07	1.0	33	93	9	42	25	330	236	2.7
	12	6.12	0.9	50	91	7	39	22	320	228	3.2
	16	5.59	3.0	45	121	3	43	18	490	366	2.6
	20	6.23	0.7	28	96	2	36	16	385	288	4.1
	24	5.99	1.2	22	70	3	33	7	310	239	3.1
	28	6.07	1.0	22	95	3	27	7	355	259	2.7
	32	5.99	1.2	28	79	3	28	8	325	245	2.6
6	0	5.39	4.8	20	110	3	14	11	353	238	1.0
	4	6.17	0.8	48	110	4	25	25	324	213	3.3
	8	6.37	0.5	40	98	4	35	13	309	211	4.2
	12	6.37	0.5	54	96	3	28	12	302	206	4.4
	16	5.77	2.0	60	160	2	33	13	421	259	5.7
	20	6.07	1.0	35	110	2	23	12	340	229	7.4
	24	5.92	1.4	28	83	2	17	5	274	190	7.7
	28	5.92	1.4	26	104	3	12	6	317	212	5.7
	32	5.96	1.3	32	90	3	15	6	305	214	3.4
7	0	5.53	3.5	25	141	5	17	9	463	319	1.0
	8	5.75	2.1	30	139	10	34	26	338	197	3.1
	16	5.39	4.8	46	175	5	33	20	395	215	5.6
	24	5.67	2.5	41	201	4	25	9	502	299	7.1
	32	5.71	2.3	38	221	4	28	7	497	274	4.7
7	0	5.47	4.0	18	100	4	16	10	441	337	1.0
	8	5.49	3.8	62	162	8	45	24	641	475	2.9
	16	5.07	10.0	63	196	7	36	23	700	494	3.7
	24	5.36	5.1	59	221	5	29	11	720	494	5.5
	32	5.50	3.7	49	238	5	31	11	675	433	4.0

APPENDIX A. Raw Uncorrected Concentrations (μeq/l) of Major Solutes

CODE	DAY	Exp pH	H	K	NH4	Cl	NO3	SO4	TotACY	WeakACY	TOC(mM)
7	0	5.39	4.8	20	110	3	14	11	353	238	1.0
	8	5.67	2.5	52	212	7	28	14	521	307	4.5
	16	5.21	7.3	56	235	5	24	12	624	382	6.4
	24	5.53	3.5	47	250	4	19	8	647	394	8.6
	32	5.64	2.7	39	263	4	21	8	610	344	5.9
8	0	5.53	3.5	25	141	5	17	9	463	319	1.0
	16	5.57	3.2	45	304	7	44	24	680	373	6.3
	32	5.58	3.1	69	451	12	51	38	795	341	7.6
8	0	5.47	4.0	18	100	4	16	10	441	337	1.0
	16	5.50	3.7	67	214	12	40	27	587	369	5.1
	32	5.51	3.6	78	340	13	45	35	736	392	6.2
8	0	5.39	4.8	20	110	3	14	11	353	238	1.0
	16	5.36	5.1	35	265	9	36	22	794	524	9.4
	32	5.40	4.7	48	442	11	39	39	911	464	10.5
9	0	7.07	0.1	108	126	11	18	5	327	201	1.0
	2	5.69	2.4	145	186	17	24	20	376	188	4.3
	4	5.89	1.5	136	132	14	53	24	356	223	5.3
	6	6.59	0.3	155	135	11	94	38	378	243	6.2
	8	6.29	0.6	129	129	9	161	23	295	165	6.8
	10	6.03	1.1	72	79	7	245	41	209	129	3.0
	12	6.47	0.4	70	68	5	262	22	204	136	2.9
	14	6.23	0.7	76	70	3	66	13	244	173	1.8
	16	5.89	1.5	80	62	3	154	7	188	125	2.4
	18	6.23	0.7	78	91	[2.3]	[133]	[6.4]	169	77	2.6
	20	6.23	0.7	61	78	3	116	5	142	63	3.3
	22	5.55	3.3	47	64	2	89	7	119	52	2.1
	24	6.29	0.6	56	82	1	72	4	157	74	3.8
	26	6.07	1.0	60	89	2	27	3	158	68	2.9
	28	6.07	1.0	60	91	1	28	6	188	96	3.6
	30	6.07	1.0	50	108	1	35	9	194	85	2.4
	32	6.12	0.9	51	97	1	36	5	169	71	2.8
9	0	7.07	0.1	97	137	11	20	5	300	163	1.0
	2	5.82	1.8	121	188	16	22	21	315	125	5.4
	4	6.29	0.6	105	179	15	45	28	221	41	6.5
	6	6.59	0.3	135	181	10	99	40	311	130	4.8
	8	6.23	0.7	108	159	8	175	25	274	114	4.6
	10	6.07	1.0	67	90	5	201	46	180	89	4.8
	12	6.29	0.6	51	80	4	211	23	176	95	4.2
	14	6.47	0.4	70	84	3	54	10	217	133	3.1
	16	6.03	1.1	48	80	3	117	7	136	55	3.7
	18	6.37	0.5	40	54	2	133	6	149	95	3.7
	20	6.29	0.6	43	55	2	101	5	123	67	3.4
	22	5.61	2.9	33	50	2	78	6	119	66	3.6
	24	6.47	0.4	48	78	2	60	3	169	91	3.7
	26	6.17	0.8	43	77	1	24	2	165	87	2.7
	28	6.12	0.9	56	85	2	26	4	167	81	2.9
	30	6.37	0.5	38	89	1	33	7	125	36	3.0
	32	6.07	1.0	19	77	1	28	4	141	63	3.1

APPENDIX A. Raw Uncorrected Concentrations (μeq/l) of Major Solutes

CODE	DAY	Exp pH	H	K	NH4	Cl	NO3	SO4	TotACY	WeakACY	TOC(mM)
9	0	7.07	0.1	86	151	6	16	2	378	227	1.0
	2	5.82	1.8	109	241	13	19	18	389	146	5.6
	4	6.07	1.0	92	187	11	39	21	338	150	5.2
	6	6.59	0.3	103	197	9	82	35	361	164	6.5
	8	6.77	0.2	96	166	7	144	20	331	165	[5.7]
	10	6.23	0.7	75	98	4	187	38	241	142	4.7
	12	6.77	0.2	77	95	3	197	20	221	126	4.2
	14	7.07	0.1	91	101	3	50	8	289	188	3.3
	16	6.07	1.0	74	89	2	98	5	201	111	4.2
	18	6.12	0.9	65	65	[2.3]	[133]	[6.4]	177	111	4.1
	20	6.17	0.8	52	69	3	89	4	155	85	5.6
	22	5.53	3.5	43	60	2	68	3	135	72	3.9
	24	6.37	0.5	52	66	[1.5]	[66.4]	[3.4]	182	116	6.1
	26	6.29	0.6	47	73	2	20	3	188	114	4.8
	28	5.92	1.4	61	79	1	23	4	200	120	5.9
	30	5.89	1.5	56	85	1	27	8	200	114	3.8
	32	6.12	0.9	56	72	0	26	3	176	103	5.9
10	0	7.07	0.1	108	126	11	18	5	327	201	1.0
	4	8.07	0.0	200	421	24	34	33	839	418	8.2
	8	6.47	0.4	164	314	14	84	44	574	260	6.6
	12	6.07	1.0	160	366	8	151	41	655	288	3.8
	16	6.47	0.4	124	175	8	200	29	330	155	4.3
	20	6.17	0.8	125	182	8	90	17	402	219	3.5
	24	5.96	1.3	85	97	6	60	22	221	123	5.3
	28	6.47	0.4	81	101	6	55	14	244	143	6.3
	32	6.47	0.4	88	89	7	79	18	239	150	3.8
10	0	7.07	0.1	97	137	11	20	5	300	163	1.0
	4	6.59	0.3	226	341	17	29	28	811	470	7.0
	8	6.23	0.7	175	265	13	73	45	479	213	6.7
	12	6.03	1.1	210	300	12	167	46	660	359	6.1
	16	6.47	0.4	144	141	9	243	40	315	174	3.8
	20	6.37	0.5	156	172	9	137	20	375	203	4.4
	24	6.23	0.7	144	88	5	78	14	207	118	5.1
	28	6.77	0.2	112	85	3	44	9	200	115	5.4
	32	6.47	0.4	115	81	6	68	11	234	153	5.4
10	0	7.07	0.1	86	151	6	16	2	378	227	1.0
	4	6.77	0.2	252	405	14	20	24	600	195	8.4
	8	7.07	0.1	192	291	11	54	30	447	156	7.0
	12	6.07	1.0	200	340	12	189	50	635	294	5.5
	16	6.29	0.6	137	170	10	278	45	255	84	4.7
	20	6.17	0.8	139	159	10	151	36	363	203	5.5
	24	5.96	1.3	131	80	5	101	19	172	91	6.8
	28	6.59	0.3	113	78	3	39	12	186	108	8.0
	32	6.77	0.2	121	64	4	63	17	190	126	6.3
11	0	7.07	0.1	108	126	11	18	5	327	201	1.0
	8	5.99	1.2	192	220	18	55	57	620	399	12.1
	16	6.03	1.1	123	168	12	259	62	375	206	7.2
	24	6.77	0.2	101	93	11	79	34	238	145	7.2
	32	6.37	0.5	86	79	12	118	39	202	123	5.8

APPENDIX A. Raw Uncorrected Concentrations (μeq/l) of Major Solutes

CODE	DAY	Exp pH	H	K	NH4	Cl	NO3	SO4	TotACY	WeakACY	TOC(mM)
11	0	7.07	0.1	97	137	11	20	5	300	163	1.0
	8	5.92	1.4	171	249	21	73	41	584	334	7.9
	16	6.03	1.1	110	195	14	238	53	360	164	6.6
	24	6.59	0.3	89	102	7	103	19	217	115	7.1
	32	6.37	0.5	70	89	7	136	34	184	95	6.7
11	0	7.07	0.1	86	151	6	16	2	378	227	1.0
	8	6.47	0.4	120	275	25	84	38	656	381	15.2
	16	6.17	0.8	100	201	18	172	40	435	233	7.9
	24	6.59	0.3	74	117	9	58	15	265	148	7.9
	32	6.77	0.2	67	105	10	97	23	247	142	7.2
12	0	7.07	0.1	108	126	11	18	5	327	201	1.0
	16	5.59	3.0	321	453	24	256	58	840	384	10.1
	32	5.59	3.0	123	211	27	321	97	416	202	9.3
12	0	7.07	0.1	97	137	11	20	5	300	163	1.0
	16	5.53	3.5	356	400	14	239	76	925	522	14.2
	32	5.61	2.9	111	196	17	256	109	435	236	10.1
12	0	7.07	0.1	86	151	6	16	2	378	227	1.0
	16	5.79	1.9	289	342	21	249	50	785	441	10.7
	32	5.57	3.2	99	163	21	278	85	319	153	11.2
13	0	7.07	0.1	108	126	11	18	5	327	201	1.0
	2	6.59	0.3	63	130	17	27	13	275	145	4.3
	4	6.47	0.4	64	125	14	31	9	347	222	4.6
	6	6.59	0.3	80	110	10	30	12	265	155	5.2
	8	6.37	0.5	82	115	7	55	10	303	188	3.1
	10	6.47	0.4	46	70	4	62	7	190	120	2.1
	12	6.47	0.4	40	60	3	59	9	162	102	1.7
	14	7.07	0.1	34	33	7	42	11	140	107	1.3
	16	7.07	0.1	25	30	2	49	4	102	72	1.5
	18	6.77	0.2	30	29	3	19	4	105	76	1.8
	20	6.77	0.2	22	31	2	15	3	110	79	1.0
	22	7.07	0.1	23	38	2	12	2	105	67	1.5
	24	6.59	0.3	22	36	3	11	2	100	64	1.6
	26	6.59	0.3	23	37	2	11	2	105	68	2.0
	28	6.59	0.3	31	39	1	13	3	127	88	1.7
	30	6.47	0.4	31	40	2	16	5	135	95	1.5
	32	6.59	0.3	37	41	1	9	2	100	59	2.0
13	0	7.07	0.1	97	137	11	20	5	300	163	1.0
	2	6.59	0.3	121	160	21	24	17	188	28	2.5
	4	6.37	0.5	105	150	12	27	13	210	60	2.4
	6	6.47	0.4	74	132	7	24	16	205	73	1.7
	8	6.37	0.5	86	145	8	38	14	208	63	1.6
	10	6.77	0.2	55	75	5	52	11	95	20	1.8
	12	6.59	0.3	38	70	3	44	11	90	20	1.6
	14	6.59	0.3	30	55	7	38	9	70	15	1.1
	16	6.77	0.2	28	47	2	45	3	53	6	1.7
	18	6.59	0.3	35	45	3	21	3	90	45	1.7
	20	6.77	0.2	27	44	2	16	2	65	21	1.2

APPENDIX A. Raw Uncorrected Concentrations (μeq/l) of Major Solutes

CODE	DAY	Exp pH	H	K	NH4	Cl	NO3	SO4	TotACY	WeakACY	TOC(mM)
13	22	6.77	0.2	27	48	2	15	2	70	22	2.1
	24	6.77	0.2	30	51	4	13	2	80	29	1.7
	26	6.59	0.3	28	54	1	11	1	70	16	1.9
	28	6.47	0.4	33	62	1	13	2	72	10	1.4
	30	6.59	0.3	35	74	2	17	3	82	8	1.5
	32	6.77	0.2	35	80	1	13	2	86	6	2.0
13	0	7.07	0.1	86	151	6	16	2	378	227	1.0
	2	7.07	0.1	140	97	18	20	19	200	103	5.2
	4	7.07	0.1	125	88	12	22	15	223	135	6.2
	6	6.77	0.2	110	82	7	23	16	193	111	6.2
	8	6.77	0.2	135	103	5	31	16	239	136	3.7
	10	6.59	0.3	85	56	3	41	16	135	79	3.7
	12	6.77	0.2	75	50	2	37	12	108	58	3.1
	14	6.77	0.2	50	38	5	32	12	90	52	2.4
	16	7.07	0.1	55	34	1	36	4	85	51	3.4
	18	6.77	0.2	58	34	2	10	5	135	101	2.6
	20	6.77	0.2	62	36	1	9	3	95	59	2.3
	22	7.07	0.1	65	43	1	9	2	80	37	2.7
	24	6.59	0.3	65	42	2	8	3	105	63	3.2
	26	6.59	0.3	64	44	1	9	3	110	66	3.6
	28	6.59	0.3	68	46	1	12	3	104	58	2.8
	30	6.59	0.3	75	48	0	11	2	110	62	2.4
	32	6.77	0.2	63	50	0	11	3	105	55	2.9
14	0	7.07	0.1	108	126	11	18	5	327	201	1.0
	4	6.77	0.2	141	371	25	35	33	595	224	6.4
	8	5.96	1.3	130	311	12	44	23	570	258	3.6
	12	6.17	0.8	85	245	10	56	23	280	34	3.5
	16	6.29	0.6	110	257	9	47	23	270	12	1.8
	20	6.37	0.5	100	208	6	33	9	320	112	2.6
	24	6.23	0.7	85	125	5	29	10	220	94	3.3
	28	6.12	0.9	80	120	5	12	3	225	104	3.2
	32	6.03	1.1	68	107	4	15	16	213	105	3.0
14	0	7.07	0.1	97	137	11	20	5	300	163	1.0
	4	7.07	0.1	230	227	19	42	38	494	267	3.9
	8	5.89	1.5	180	140	12	50	32	430	289	3.7
	12	6.37	0.5	145	128	9	60	35	200	72	2.8
	16	6.37	0.5	165	139	7	55	28	220	81	2.9
	20	6.23	0.7	170	132	4	36	12	290	157	2.8
	24	6.29	0.6	145	70	3	32	8	215	144	3.2
	28	6.29	0.6	130	86	4	14	4	220	133	2.4
	32	6.12	0.9	126	70	8	24	29	175	104	2.5
14	0	7.07	0.1	86	151	6	16	2	378	227	1.0
	4	6.77	0.2	130	275	14	24	44	861	586	6.5
	8	6.29	0.6	140	170	10	40	33	750	579	4.3
	12	6.47	0.4	100	141	8	47	36	525	384	4.6
	16	6.37	0.5	148	147	8	43	31	610	463	3.7
	20	6.47	0.4	120	155	5	28	13	440	285	4.1
	24	6.37	0.5	94	99	5	25	10	285	186	4.4
	28	6.29	0.6	75	97	4	11	4	305	207	4.2
	32	6.17	0.8	82	84	6	15	19	245	160	3.8

APPENDIX A. Raw Uncorrected Concentrations (μeq/l) of Major Solutes

CODE	DAY	Exp pH	H	K	NH4	Cl	NO3	SO4	TotACY	WeakACY	TOC(mM)
15	0	7.07	0.1	108	126	11	18	5	327	201	1.0
	8	6.59	0.3	194	180	12	44	25	305	125	3.8
	16	6.59	0.3	145	148	8	41	24	260	112	3.2
	24	6.47	0.4	117	111	9	36	19	190	79	4.1
	32	6.47	0.4	120	112	8	45	22	180	68	3.3
15	0	7.07	0.1	97	137	11	20	5	300	163	1.0
	8	6.77	0.2	132	241	14	58	30	375	134	3.4
	16	6.37	0.5	90	129	9	48	31	315	186	2.6
	24	6.37	0.5	68	70	9	33	18	225	155	3.5
	32	6.59	0.3	82	95	8	44	20	204	109	3.4
15	0	7.07	0.1	86	151	6	16	2	378	227	1.0
	8	6.37	0.5	118	203	15	65	44	340	137	5.0
	16	6.47	0.4	80	110	10	54	29	325	215	4.5
	24	6.47	0.4	52	86	6	25	19	275	189	4.5
	32	6.37	0.5	62	75	0	29	23	252	177	4.3
16	0	7.07	0.1	108	126	11	18	5	327	201	1.0
	16	6.37	0.5	65	99	20	65	27	265	166	2.8
	32	6.17	0.8	196	112	22	104	43	360	247	3.9
16	0	7.07	0.1	97	137	11	20	5	300	163	1.0
	16	6.23	0.7	118	154	18	72	34	370	215	2.9
	32	5.99	1.2	256	178	20	121	58	539	360	3.6
16	0	7.07	0.1	86	151	6	16	2	378	227	1.0
	16	6.47	0.4	81	110	15	57	42	355	245	4.3
	32	6.12	0.9	211	133	16	84	64	445	311	5.0
17	2	4.28	62.0	[154]	[775]	[8.7]	[228]	[8.8]	[2508]	[1671]	[34.8]
	4	4.81	18.4	120	640	12	181	5	1000	342	32.2
	6	5.09	9.6	100	207	13	95	5	440	223	14.7
	8	5.12	8.9	88	120	6	102	6	360	231	11.5
	10	5.18	7.8	44	77	7	31	7	270	185	9.7
17	2	4.45	41.7	165	720	10	195	9	2715	1953	36.3
	4	5.09	9.6	151	690	8	126	7	1415	715	36.3
	6	4.83	17.4	142	309	12	88	2	700	374	23.5
	8	5.01	11.4	116	186	8	75	1	485	288	14.1
	10	5.36	5.1	61	98	9	51	2	375	272	14.4
17	2	4.66	26.0	142	830	8	262	8	2300	1444	33.2
	4	5.50	3.7	120	450	6	147	10	950	496	28.2
	6	5.18	7.7	108	148	9	62	4	550	394	21.6
	8	5.11	9.1	120	142	4	88	[3.3]	460	309	16.7
	10	5.38	4.9	47	101	5	45	2	340	234	12.2
18	2	4.55	32.9	221	680	12	340	8	2390	1677	30.4
	4	4.91	14.4	86	318	9	191	5	1100	768	32.4
	6	5.02	11.2	79	181	12	102	5	560	368	19.5
	8	[5.17]	[8]	[46]	[139]	[7.1]	[98]	[2.7]	[465]	[318]	[14.5]
	10	5.25	6.6	44	121	4	88	2	340	212	10.1

APPENDIX A. Raw Uncorrected Concentrations (μeq/l) of Major Solutes

CODE	DAY	Exp pH	H	K	NH4	Cl	NO3	SO4	TotACY	WeakACY	TOC(mM)
18	2	4.57	31.9	183	770	12	202	9	2465	1663	36.1
	4	4.98	12.2	104	339	14	176	11	1440	1089	38.6
	6	5.07	9.9	56	208	8	84	2	660	442	21.8
	8	5.15	8.4	43	136	10	94	3	490	346	15.3
	10	5.31	5.7	38	110	8	57	3	410	294	13.0
18	2	4.56	32.2	202	728	15	165	6	2590	1830	35.4
	4	5.35	5.3	98	250	9	142	9	1125	870	37.3
	6	5.01	11.6	66	242	9	96	4	620	366	20.4
	8	5.18	7.7	49	142	4	102	2	440	290	13.6
	10	5.35	5.3	40	89	6	46	1	335	241	9.6
19	2	4.57	32.0	[183]	[812]	14	379	14	2000	1156	35.3
	4	5.05	10.4	142	308	5	66	3	880	562	28.5
	6	4.91	14.6	68	204	7	131	8	740	521	19.6
	8	5.29	6.1	48	108	8	77	5	420	306	12.2
	10	5.31	5.8	44	102	8	22	3	350	242	8.6
19	2	4.52	35.9	202	920	16	198	10	2900	1944	37.8
	4	4.79	19.3	121	321	7	195	6	1000	660	34.2
	6	5.01	11.6	72	200	9	122	11	700	488	18.0
	8	4.95	13.2	48	111	7	44	3	460	336	13.4
	10	5.17	8.0	48	96	3	56	[3.9]	380	276	10.7
19	2	4.61	29.1	165	704	9	229	13	2350	1617	40.3
	4	4.73	21.9	88	281	10	162	6	845	542	29.8
	6	4.83	17.4	51	141	[8]	98	5	560	402	15.6
	8	5.09	9.6	51	96	6	41	7	410	304	11.9
	10	5.24	6.7	36	71	8	46	5	335	257	6.4
20	2	5.18	7.8	161	624	6	133	16	1350	718	10.3
	4	5.15	8.3	131	424	15	124	6	1000	568	5.9
	6	5.07	9.9	88	306	15	120	4	660	344	4.7
	8	5.21	7.3	52	211	6	101	3	450	232	4.7
	10	5.50	3.7	29	206	5	161	4	430	220	3.6
20	2	5.00	11.9	158	538	6	193	16	1250	700	8.1
	4	5.41	4.6	148	462	18	193	8	1240	773	7.2
	6	5.44	4.3	78	330	6	171	6	700	366	5.2
	8	5.15	8.3	48	271	17	115	5	645	366	5.7
	10	5.19	7.6	33	211	6	137	6	450	231	4.0
20	2	[5.07]	[9.9]	[160]	[581]	[5.8]	[163]	[16.1]	[1300]	[709.1]	[9.2]
	4	5.25	6.6	193	724	23	27	14	1650	919	9.3
	6	5.12	9.0	108	420	5	[145]	9	1120	691	9.2
	8	5.07	9.9	56	394	18	300	6	830	426	6.4
	10	5.14	8.5	42	288	7	223	6	660	364	6.2
21	2	5.11	9.2	164	593	2	151	31	1030	428	7.2
	4	5.08	9.7	106	221	8	138	43	510	279	5.7
	6	4.98	12.2	98	242	7	105	40	515	261	4.9
	8	5.31	5.8	88	211	6	88	40	490	273	4.8
	10	5.79	1.9	56	109	2	176	41	390	279	4.4

APPENDIX A. Raw Uncorrected Concentrations ($\mu eq/l$) of Major Solutes

CODE	DAY	Exp pH	H	K	NH4	Cl	NO3	SO4	TotACY	WeakACY	TOC(mM)
21	2	5.54	3.4	179	618	3	148	39	1200	579	8.8
	4	4.83	17.6	148	437	7	124	39	930	475	6.0
	6	4.89	15.2	107	261	4	142	40	600	324	4.8
	8	5.10	9.3	97	229	5	181	43	515	277	4.9
	10	5.09	9.6	58	121	2	103	41	450	319	3.9
21	2	5.12	8.9	226	814	5	196	48	1640	817	13.1
	4	5.66	2.6	182	629	5	176	44	1340	708	9.9
	6	5.12	8.9	148	498	2	156	35	1120	613	9.3
	8	5.05	10.4	129	391	6	126	33	850	449	8.0
	10	5.18	7.8	77	201	2	192	33	690	481	4.6
22	2	5.15	8.4	202	621	4	239	91	1420	791	9.8
	4	5.19	7.6	191	488	5	148	106	1340	844	8.4
	6	4.84	17.2	136	391	7	133	103	980	572	7.3
	8	5.01	11.5	83	304	7	216	95	790	475	6.3
	10	4.94	13.5	69	281	2	199	94	650	356	4.9
22	2	5.31	5.7	188	507	4	277	78	1330	817	8.8
	4	4.99	12.0	156	388	2	154	116	1050	650	6.1
	6	5.07	9.9	149	286	6	148	105	800	504	5.5
	8	5.29	6.0	45	167	8	177	102	490	317	5.5
	10	5.44	4.3	41	107	2	142	107	320	209	3.9
22	2	5.00	11.7	164	451	2	176	93	1000	537	6.2
	4	4.98	12.2	83	182	2	158	110	550	356	[7.3]
	6	5.16	8.1	69	136	5	198	101	400	256	5.5
	8	5.02	11.2	56	155	6	130	124	460	294	5.3
	10	5.24	6.7	48	124	2	101	119	450	319	4.0
23	2	4.93	13.7	78	366	5	173	3	830	450	7.4
	4	4.62	28.3	121	479	12	65	6	1200	693	8.6
	6	4.56	32.5	166	236	9	25	5	1125	857	6.2
	8	4.54	33.6	198	425	[10.7]	325	4	980	521	4.4
	10	4.39	48.0	371	243	8	271	3	900	609	4.3
23	2	5.17	8.0	56	328	12	133	5	900	564	9.8
	4	5.32	5.6	83	221	8	101	4	700	473	10.3
	6	4.76	20.3	167	284	[9.4]	141	7	1200	896	7.3
	8	4.91	14.5	168	360	17	281	2	1125	751	4.7
	10	4.84	17.0	271	307	12	246	3	960	636	6.8
23	2	5.01	11.4	81	395	6	198	5	880	474	5.8
	4	5.04	10.8	88	398	12	48	7	1130	721	6.3
	6	4.94	13.6	188	263	[9.4]	163	5	730	453	3.8
	8	5.71	2.3	88	121	4	272	3	560	437	2.7
	10	4.82	18.0	471	524	5	393	3	1600	1058	1.3
24	2	5.03	11.0	116	426	9	189	5	940	503	6.0
	4	5.58	3.1	140	502	45	475	18	1350	845	8.3
	6	5.61	2.9	151	971	33	492	13	1500	526	9.6
	8	5.53	3.5	124	844	124	625	28	1400	553	7.1
	10	5.28	6.2	129	966	77	481	17	1390	418	6.4

APPENDIX A. Raw Uncorrected Concentrations (μeq/l) of Major Solutes

CODE	DAY	Exp pH	H	K	NH4	Cl	NO3	SO4	TotACY	WeakACY	TOC(mM)
24	2	5.30	5.9	89	366	12	85	5	825	453	7.3
	4	5.47	4.0	160	488	52	443	18	1425	933	13.3
	6	5.87	1.6	138	1021	40	205	18	1700	677	13.3
	8	5.27	6.3	122	908	82	343	18	1625	711	13.6
	10	6.03	1.1	242	721	57	296	12	1060	338	12.6
24	2	5.18	7.7	97	402	8	137	3	842	432	8.3
	4	5.82	1.8	165	526	61	209	23	1700	1172	12.8
	6	5.67	2.5	167	874	224	654	30	2375	1499	13.8
	8	5.71	2.3	166	808	84	528	[23.2]	1525	715	14.5
	10	5.99	1.2	188	790	61	323	10	1260	469	30.7
25	2	5.69	2.4	110	126	14	274	3	640	512	4.8
	4	5.71	2.3	88	207	5	221	3	500	291	3.9
	6	6.47	0.4	67	228	9	224	3	300	72	0.0
	8	5.53	3.5	38	176	5	183	3	450	271	3.1
	10	5.99	1.2	25	111	2	142	3	400	288	3.3
25	2	5.73	2.2	105	160	9	221	3	500	338	4.0
	4	6.17	0.8	77	202	8	188	1	250	47	3.4
	6	5.92	1.4	55	188	[9.3]	188	2	380	191	3.3
	8	6.03	1.1	28	106	4	84	1	250	143	3.3
	10	6.59	0.3	20	88	3	108	1	240	152	3.3
25	2	6.29	0.6	164	134	[11.5]	241	3	460	325	4.1
	4	6.23	0.7	116	254	4	152	2	340	85	4.1
	6	6.59	0.3	48	108	9	121	4	240	132	20.8
	8	5.89	1.5	32	142	[4.3]	109	2	350	207	3.3
	10	6.23	0.7	17	69	4	121	1	160	90	3.2
26	2	5.47	4.0	121	308	9	322	10	600	288	4.1
	4	5.51	3.6	173	411	24	419	21	1500	1085	7.9
	6	5.96	1.3	92	188	33	604	16	1800	1611	9.8
	8	5.71	2.3	88	166	39	625	18	1900	1732	5.7
	10	5.82	1.8	64	191	15	398	11	1160	967	3.8
26	2	6.17	0.8	145	273	7	254	11	560	286	6.6
	4	6.37	0.5	203	378	39	379	23	1900	1522	9.4
	6	5.96	1.3	121	198	52	498	21	1660	1461	16.8
	8	6.29	0.6	77	121	35	600	22	1800	1678	13.3
	10	5.84	1.7	103	300	22	487	6	2000	1698	7.8
26	2	5.96	1.3	208	176	8	351	2	500	323	0.0
	4	6.17	0.8	105	194	24	544	16	1200	1005	9.6
	6	5.96	1.3	131	204	33	654	23	2750	2545	13.3
	8	6.17	0.8	80	111	9	524	17	1600	1488	8.3
	10	6.29	0.6	69	177	15	399	11	1350	1172	5.8
27	2	4.77	19.8	138	584	10	304	10	1304	700	10.4
	4	4.54	33.8	[100]	[458]	22	467	22	1861	1369	27.5
	6	4.48	38.7	179	821	23	237	8	1911	1051	13.7

APPENDIX A. Raw Uncorrected Concentrations (μeq/l) of Major Solutes

CODE	DAY	Exp pH	H	K	NH4	Cl	NO3	SO4	TotACY	WeakACY	TOC(mM)
27	2	4.83	17.6	117	446	17	246	13	1203	739	10.8
	4	4.84	16.9	121	504	9	211	6	1219	698	9.2
	6	4.82	17.9	88	426	11	136	4	938	494	5.5
27	2	5.01	11.5	159	526	14	331	6	1425	888	12.8
	4	4.88	15.6	79	413	7	188	5	1143	714	8.6
	6	4.67	25.2	106	539	18	231	7	1436	872	11.5
28	2	4.83	17.4	141	507	10	221	8	996	472	4.2
	4	4.73	21.7	98	436	14	243	15	1149	691	10.0
	6	[4.77]	[19.9]	[79]	[359]	[10]	[223]	[15.7]	[1006]	[627.1]	[10.3]
28	2	5.09	9.6	188	687	9	291	9	1427	730	8.1
	4	4.94	13.4	86	411	9	207	12	1070	646	8.9
	6	4.78	19.7	69	374	11	214	20	998	604	11.0
28	2	5.16	8.2	77	388	8	208	7	973	577	8.5
	4	4.90	14.8	94	454	8	301	12	1126	657	9.2
	6	4.77	20.1	88	344	9	233	12	1009	645	9.6
29	2	4.91	14.6	79	394	11	165	3	855	446	5.5
	4	4.62	28.4	108	488	10	221	8	1386	870	12.5
	6	4.54	33.6	108	443	14	256	11	1225	748	11.1
29	2	5.10	9.3	88	463	8	124	6	1104	632	9.3
	4	5.01	11.6	121	562	4	104	9	1421	847	12.2
	6	4.82	17.9	122	409	10	154	10	1200	773	10.7
29	2	4.97	12.7	56	421	9	129	6	920	486	5.7
	4	4.87	15.9	87	403	6	146	10	1143	724	10.7
	6	4.68	24.3	92	326	12	203	10	1020	670	9.4
30	2	4.89	15.2	108	488	14	245	3	1108	605	7.7
	4	4.85	16.7	124	603	17	241	10	1421	801	11.0
	6	4.60	29.6	78	326	20	156	12	880	524	4.7
30	2	4.83	17.3	126	573	18	260	6	1342	752	9.7
	4	4.87	15.8	109	543	12	208	6	1398	839	11.4
	6	4.79	19.3	126	481	14	126	14	1342	842	7.3
30	2	5.15	8.4	71	401	11	200	9	961	552	6.6
	4	4.99	12.1	125	496	9	233	10	1261	753	10.3
	6	4.88	15.4	149	637	13	303	10	1511	859	11.2
31	2	4.93	13.8	81	388	8	137	4	898	496	5.5
	4	4.92	14.2	101	429	15	229	4	1107	664	6.0
	6	4.66	25.6	121	521	14	176	6	1341	794	10.5
31	2	5.13	8.7	66	337	6	111	8	721	375	2.6
	4	4.96	12.9	83	454	10	204	12	1004	537	5.7
	6	4.78	19.4	79	367	9	108	7	970	584	8.2

APPENDIX A. Raw Uncorrected Concentrations ($\mu eq/l$) of Major Solutes

CODE	DAY	Exp pH	H	K	NH4	Cl	NO3	SO4	TotACY	WeakACY	TOC(mM)
31	2	5.26	6.4	43	211	11	88	11	536	319	2.4
	4	5.03	11.0	56	207	6	149	14	698	480	3.6
	6	4.74	21.5	94	419	12	121	10	1109	669	9.5
32	2	5.99	1.2	98	105	12	138	16	640	534	7.7
	4	6.12	0.9	108	88	14	148	17	575	486	4.4
	6	5.71	2.3	121	127	9	159	21	721	592	5.5
32	2	6.59	0.3	84	126	14	175	9	465	339	3.1
	4	5.89	1.5	121	96	9	126	11	403	306	1.6
	6	5.55	3.3	137	136	8	146	17	675	536	5.0
32	2	6.37	0.5	111	105	10	143	8	588	483	2.7
	4	5.84	1.7	143	103	11	118	12	391	286	1.3
	6	5.53	3.5	148	133	11	186	15	638	502	4.8
33	2	6.17	0.8	88	125	6	171	13	505	379	3.3
	4	5.84	1.7	124	106	9	133	13	525	417	3.5
	6	5.39	4.8	134	176	9	191	16	621	440	6.1
33	2	5.89	1.5	121	131	8	159	16	475	343	2.6
	4	5.73	2.2	151	127	10	171	14	542	413	3.3
	6	5.32	5.6	111	106	11	203	14	705	593	9.3
33	2	5.99	1.2	117	154	8	163	9	442	287	1.2
	4	5.57	3.2	176	142	10	146	12	506	361	4.9
	6	5.79	1.9	142	111	8	186	12	600	487	6.9
34	2	5.75	2.1	110	128	8	139	12	520	390	4.7
	4	6.07	1.0	124	121	8	148	13	650	528	5.5
	6	5.39	4.8	104	142	9	181	12	725	578	7.8
34	2	5.62	2.8	126	139	7	176	17	440	298	3.7
	4	5.79	1.9	106	91	7	171	10	390	297	2.6
	6	5.32	5.6	77	161	8	154	13	648	481	6.8
34	2	5.67	2.5	88	164	7	154	16	496	330	4.1
	4	5.53	3.5	97	97	7	125	9	445	345	2.8
	6	5.44	4.3	91	124	7	203	14	540	412	6.0
35	2	6.37	0.5	107	128	9	157	16	640	512	7.3
	4	5.69	2.4	76	171	7	126	14	500	327	4.3
	6	5.89	1.5	101	191	9	191	21	590	398	5.7
35	2	5.82	1.8	126	134	7	169	19	525	389	5.7
	4	6.23	0.7	100	156	8	188	15	407	250	1.4
	6	6.07	1.0	121	184	5	209	15	565	380	5.3
35	2	6.23	0.7	89	146	8	177	17	581	434	5.9
	4	6.17	0.8	94	177	4	154	17	442	264	7.1
	6	5.77	2.0	116	199	6	177	13	525	324	5.2

APPENDIX A. Raw Uncorrected Concentrations (μeq/l) of Major Solutes

CODE	DAY	Exp pH	H	K	NH4	Cl	NO3	SO4	TotACY	WeakACY	TOC(mM)
36	2	6.03	1.1	98	104	6	143	9	495	390	6.1
	4	5.89	1.5	111	121	9	144	16	380	258	3.6
	6	5.75	2.1	126	202	11	167	20	750	546	7.6
36	2	5.84	1.7	75	79	5	121	12	565	484	7.2
	4	5.77	2.0	78	141	8	118	13	438	295	1.6
	6	5.64	2.7	108	188	10	154	15	690	499	7.1
36	2	5.69	2.4	85	56	8	107	8	425	367	2.3
	4	6.17	0.8	97	156	8	142	13	505	348	5.3
	6	5.57	3.2	100	221	10	112	13	820	596	7.9

APPENDIX B. Averages and Standard Deviations (μeq/kg litter) of Major Solutes

CODE	DAY	HYDROGEN		POTASSIUM		AMMONIUM		CHLORIDE		NITRATE		SULFATE		TOT. ACIDITY		WEAK ACIDITY		TOC (MMOL/L)	
		Avg	Std	Avg	Std	Avg	Std	Avg	Std	Avg	Std	Avg	Std	Avg	Std	Avg	Std	Avg	Std
1	0	4.0	1	36	7	200	41	-15	2	7	2	-2	2	770	111	566	100	1.9	0
	2	9.3	1	112	23	593	51	-11	3	44	13	3	4	3257	435	2654	385	20.3	4
	4	9.7	2	67	12	334	47	-17	1	100	6	11	4	1385	57	1041	56	11.5	1
	6	6.3	1	70	7	363	74	-16	1	184	21	25	5	1759	126	1390	112	8.9	1
	8	8.7	1	40	10	236	68	-18	1	207	40	16	8	1191	85	946	107	9.1	1
	10	8.7	1	34	7	251	41	-20	1	144	14	13	6	1053	95	793	89	8.2	1
	12	6.5	1	30	8	209	65	-19	1	126	25	3	2	965	85	750	75	6.0	1
	14	19.4	7	29	7	186	69	-18	1	130	10	-2	3	809	131	604	84	5.2	1
	16	31.7	6	19	4	167	19	-17	1	230	25	7	4	638	130	439	116	6.0	1
	18	25.5	5	15	7	125	40	-13	2	182	25	11	4	505	93	355	67	5.6	1
	20	28.5	7	11	4	120	21	-15	2	150	12	8	5	600	125	452	109	4.6	1
	22	15.2	4	8	3	95	27	-17	1	124	23	4	4	371	55	260	63	3.0	1
	24	13.3	4	6	2	76	11	-19	1	65	7	-4	4	241	27	152	12	4.7	1
	26	5.7	2	6	4	82	11	-19	1	80	15	-13	2	258	32	171	20	4.4	2
	28	19.0	4	4	2	78	16	-20	0	43	4	-13	2	315	51	219	32	3.6	2
	30	1.9	3	4	2	84	11	-19	1	51	7	-15	1	296	45	211	31	2.4	1
	32	5.3	1	2	0	57	23	-18	0	62	5	-11	2	287	34	225	11	3.1	1
2	0	4.0	1	36	7	200	41	-15	2	7	2	-2	2	770	111	566	100	1.9	0
	4	27.5	7	201	29	982	64	-5	4	64	8	25	12	4161	659	3151	607	31.9	15
	8	31.4	4	80	15	587	109	-11	2	149	32	33	6	1792	335	1173	259	12.9	6
	12	69.9	10	57	20	372	34	-13	1	228	26	42	12	1227	224	785	197	8.4	3
	16	64.8	13	36	7	184	28	-14	2	257	41	33	5	543	47	294	39	5.6	1
	20	34.2	4	32	7	108	18	-16	1	217	40	21	6	416	40	274	28	5.0	2
	24	35.5	11	27	4	114	25	-17	2	150	25	13	4	439	51	289	50	4.8	2
	28	45.6	7	17	7	120	27	-17	1	96	25	6	6	462	37	296	50	5.0	2
	32	55.1	7	11	3	131	19	-17	1	120	18	12	11	526	93	340	97	3.5	1
3	0	4.0	1	36	7	200	41	-15	2	7	2	-2	2	770	111	566	100	1.9	0
	8	68.4	11	331	22	1670	212	1	2	188	31	42	7	6549	618	4811	637	27.2	4
	16	153.7	27	99	21	602	54	-6	2	249	25	62	10	1917	83	1161	73	12.0	1
	24	110.2	29	65	11	407	42	-11	3	149	17	36	16	980	122	464	119	8.4	3
	32	131.1	28	82	20	464	46	-9	0	181	19	41	22	933	203	338	136	4.0	1
4	0	4.0	1	36	7	200	41	-15	2	7	2	-2	2	770	111	566	100	1.9	0
	16	103.9	26	448	127	2801	173	9	4	270	27	86	19	7423	1275	4519	1145	12.1	4
	32	151.4	65	397	46	1853	85	15	11	405	52	103	27	3059	433	1055	431	5.8	1
5	0	4.0	1	36	7	200	41	-15	2	7	2	-2	2	770	111	566	100	1.9	0
	2	1.3	0	103	23	348	87	-6	4	18	9	6	4	1474	457	1125	372	4.4	1
	4	-1.3	1	70	24	274	72	1	5	41	12	17	5	847	206	575	142	11.2	1
	6	-2.1	0	30	14	182	56	-14	1	25	11	18	6	671	199	490	142	5.9	1
	8	-3.0	0	25	10	144	40	-19	1	19	6	10	10	467	160	326	122	4.9	1
	10	-1.0	1	21	10	163	55	-19	0	12	6	3	5	633	140	470	84	5.8	1
	12	-3.2	0	17	7	146	31	-20	1	28	27	-4	5	555	136	412	166	5.3	2
	14	-3.4	0	13	5	120	29	-18	2	4	3	-10	3	429	72	313	93	5.4	1
	16	-1.1	1	27	8	222	31	-14	2	-4	16	-2	5	727	152	506	168	4.8	2
	18	-3.4	0	10	6	131	49	-16	1	55	22	3	8	448	102	321	127	7.0	3
	20	-2.6	0	10	3	144	47	-19	1	36	21	-6	4	473	103	331	128	3.5	1
	22	-2.9	0	8	2	135	58	-19	0	46	7	-8	4	477	109	345	125	4.1	2
	24	-2.8	0	8	0	125	42	-17	1	81	17	-10	2	481	94	358	108	5.9	2
	26	-3.3	0	6	2	101	22	-19	0	16	13	-13	3	429	104	332	111	6.0	2

APPENDIX B. Averages and Standard Deviations (μeq/kg litter) of Major Solutes

CODE	DAY	HYDROGEN		POTASSIUM		AMMONIUM		CHLORIDE		NITRATE		SULFATE		TOT. ACIDITY		WEAK ACIDITY		TOC (MMOL/L)	
		Avg	Std	Avg	Std	Avg	Std	Avg	Std	Avg	Std	Avg	Std	Avg	Std	Avg	Std	Avg	Std
5	28	-2.1	1	4	1	87	15	-20	0	0	6	-13	3	479	79	393	88	4.8	2
	30	-2.7	0	6	1	120	28	-20	1	2	6	-13	2	443	34	326	62	3.3	0
	32	-2.8	0	3	1	105	16	-20	1	9	4	-11	3	466	50	364	64	3.6	1
6	0	4.0	1	36	7	200	41	-15	2	7	2	-2	2	770	111	566	100	1.9	0
	4	-2.0	0	87	36	184	14	-11	5	34	9	29	9	728	144	545	137	5.3	1
	8	-2.3	0	70	11	167	16	-11	4	49	7	14	11	618	67	453	55	6.1	2
	12	-2.4	0	99	8	163	16	-12	4	41	10	10	9	589	46	428	35	6.8	1
	16	2.9	3	112	31	266	53	-18	1	49	10	9	5	918	152	649	139	7.5	3
	20	-2.3	0	70	26	190	32	-19	1	34	13	6	4	752	162	565	139	9.6	4
	24	-0.8	1	55	21	144	40	-18	1	26	16	-8	3	616	155	472	122	10.4	4
	28	-1.0	1	51	17	182	29	-18	0	15	13	-9	1	684	130	503	106	8.0	3
	32	-1.0	1	63	17	154	30	-17	1	20	14	-8	2	635	111	482	86	5.2	1
7	0	4.0	1	36	7	200	41	-15	2	7	2	-2	2	770	111	566	100	1.9	0
	8	1.5	2	87	31	302	71	-7	2	45	16	20	12	923	290	620	266	6.6	2
	16	10.2	5	101	16	361	58	-12	3	36	11	14	11	1062	302	691	267	9.9	3
	24	3.2	2	89	17	403	47	-15	1	23	10	-3	2	1157	211	751	186	13.4	3
	32	1.7	1	76	12	434	40	-15	1	27	10	-5	4	1102	171	666	152	9.2	2
8	0	4.0	1	36	7	200	41	-15	2	7	2	-2	2	770	111	566	100	1.9	0
	16	3.8	2	89	31	473	86	-6	4	53	7	25	4	1279	197	802	168	13.2	4
	32	3.4	2	120	29	758	117	-0	2	63	12	50	3	1520	169	758	118	15.4	4
9	0	-3.6	0	181	21	239	24	-5	5	11	4	-13	3	610	75	374	61	1.9	0
	2	0.0	1	234	35	367	59	6	4	19	5	16	3	657	75	291	60	9.7	1
	4	-1.8	1	207	43	293	56	2	4	64	13	25	7	553	139	262	173	10.8	1
	6	-3.2	0	245	50	302	61	-4	2	151	17	51	5	638	66	340	110	11.1	2
	8	-2.9	1	207	32	265	37	-8	2	281	29	22	5	543	55	282	56	7.2	7
	10	-2.0	0	132	8	146	18	-13	2	378	58	58	7	372	58	228	53	7.9	2
	12	-3.0	0	122	26	131	26	-15	2	402	65	21	3	354	43	226	40	7.2	1
	14	-3.0	1	146	21	139	29	-17	0	85	16	-1	4	448	69	313	54	5.2	2
	16	-1.5	1	124	32	124	26	-18	1	211	54	-8	2	306	65	184	70	6.5	2
	18	-2.5	0	112	37	110	36	-21	3	61	146	-17	7	287	27	179	32	6.6	1
	20	-2.5	0	95	17	105	22	-17	1	171	26	-12	2	239	31	137	22	7.8	2
	22	2.3	1	74	14	87	14	-19	1	126	20	-11	4	210	18	120	19	6.1	2
	24	-2.9	0	95	8	120	16	-21	2	61	74	-17	4	295	24	178	39	8.6	3
	26	-2.3	0	91	17	129	16	-20	1	22	6	-16	0	297	30	171	44	6.6	2
	28	-1.7	1	108	5	139	11	-21	1	26	5	-12	2	325	32	188	37	7.9	3
	30	-1.9	1	87	17	156	23	-21	1	37	8	-6	2	302	79	148	75	5.8	1
	32	-2.0	0	76	38	133	25	-21	1	34	10	-14	1	281	35	150	40	7.5	3
10	0	-3.6	0	181	21	239	24	-5	5	11	4	-13	3	610	75	374	61	1.9	0
	4	-3.5	0	426	49	716	80	12	10	30	13	33	9	1398	248	686	278	14.9	1
	8	-3.0	1	333	27	528	47	1	3	110	29	54	15	923	126	398	99	12.9	0
	12	-1.8	0	357	50	614	63	-3	5	298	36	66	8	1208	25	596	75	9.8	2
	16	-2.9	0	253	19	285	35	-6	2	434	74	51	16	543	75	261	89	8.1	1
	20	-2.5	0	262	29	302	22	-6	2	217	61	25	19	695	38	396	18	8.5	2
	24	-1.7	1	224	59	145	16	-13	1	128	39	14	8	353	48	210	33	10.9	2
	28	-3.2	0	190	35	144	22	-15	3	64	15	1	5	372	58	231	35	12.5	3
	32	-3.2	0	201	33	125	24	-12	3	110	16	8	7	393	51	271	28	9.8	2

APPENDIX B. Averages and Standard Deviations (μeq/kg litter) of Major Solutes

CODE	DAY	HYDROGEN		POTASSIUM		AMMONIUM		CHLORIDE		NITRATE		SULFATE		TOT. ACIDITY		WEAK ACIDITY		TOC (MMOL/L)	
		Avg	Std	Avg	Std	Avg	Std	Avg	Std	Avg	Std	Avg	Std	Avg	Std	Avg	Std	Avg	Std
11	0	-3.6	0	181	21	239	24	-5	5	11	4	-13	3	610	75	374	61	1.9	0
	8	-1.9	1	302	70	448	52	18	7	111	27	65	19	1151	68	705	64	22.3	7
	16	-1.9	0	207	22	334	33	5	6	401	86	77	22	714	75	382	66	13.7	1
	24	-3.3	0	163	26	175	23	-6	3	129	43	22	19	429	46	258	35	14.1	1
	32	-3.0	0	137	19	150	25	-5	4	200	37	39	15	374	62	227	45	12.5	1
12	0	-3.6	0	181	21	239	24	-5	5	11	4	-13	3	610	75	374	61	1.9	0
	16	1.5	2	608	64	734	105	15	9	448	16	96	25	1588	134	853	131	22.2	4
	32	2.0	0	207	23	338	47	18	10	519	63	163	23	714	118	374	80	19.4	2
13	0	-3.6	0	181	21	239	24	-5	5	11	4	-13	3	610	75	374	61	1.9	0
	2	-3.4	0	201	76	222	60	13	5	22	7	10	6	393	90	174	113	7.6	3
	4	-3.2	0	182	59	207	59	2	2	28	9	2	5	467	144	263	154	8.4	4
	6	-3.2	0	163	37	182	48	-8	3	26	7	7	4	393	73	214	78	8.3	4
	8	-3.0	0	188	56	207	41	-10	3	56	23	4	6	448	92	244	119	5.3	2
	10	-3.2	0	114	39	105	19	-15	2	75	21	1	9	239	91	138	95	4.8	2
	12	-3.2	0	93	40	91	19	-18	1	66	21	-1	3	201	71	113	78	4.1	2
	14	-3.4	0	68	20	57	22	-11	3	49	10	-1	3	163	69	110	88	3.0	1
	16	-3.5	0	65	31	48	17	-19	1	59	13	-14	1	125	47	81	64	4.2	2
	18	-3.4	0	74	28	46	16	-18	1	9	11	-14	2	182	44	140	53	3.9	1
	20	-3.4	0	67	41	48	12	-19	1	2	8	-16	1	144	44	100	56	2.9	1
	22	-3.5	0	69	44	59	10	-20	1	0	6	-17	1	135	34	80	44	4.0	1
	24	-3.3	0	70	43	59	14	-17	2	-3	4	-17	1	154	25	98	38	4.1	2
	26	-3.2	0	69	43	63	16	-21	1	-3	2	-17	2	154	41	94	56	4.8	2
	28	-3.2	0	80	40	70	22	-21	1	1	1	-16	1	165	52	98	75	3.7	1
	30	-3.2	0	86	46	80	34	-21	2	5	6	-15	3	181	50	104	83	3.4	1
	32	-3.4	0	82	30	86	39	-21	1	-2	4	-17	2	158	19	76	56	4.4	1
14	0	-3.6	0	181	21	239	24	-5	5	11	4	-13	3	610	75	374	61	1.9	0
	4	-3.5	0	314	104	530	139	14	10	41	17	51	10	1208	360	682	376	10.6	3
	8	-1.6	1	281	50	371	174	-1	2	62	10	35	10	1082	305	713	337	7.3	1
	12	-2.7	0	205	59	303	122	-6	2	80	13	39	14	610	322	310	365	6.9	2
	16	-2.8	0	264	54	321	125	-8	2	69	12	30	8	670	403	352	461	5.3	2
	20	-2.8	0	243	69	291	74	-13	2	39	8	1	4	638	151	350	170	6.0	2
	24	-2.7	0	201	61	163	52	-15	3	32	7	-3	2	429	74	269	87	6.9	1
	28	-2.5	0	177	58	169	33	-15	1	1	3	-14	2	448	91	282	101	6.2	2
	32	-2.0	0	171	58	143	35	-12	4	11	9	20	14	374	67	234	61	5.9	1
15	0	-3.6	0	181	21	239	24	-5	5	11	4	-13	3	610	75	374	61	1.9	0
	8	-3.2	0	277	77	372	59	3	3	83	21	42	19	619	67	250	12	7.7	2
	16	-3.0	0	196	67	222	36	-6	2	68	13	32	7	543	67	324	101	6.5	2
	24	-3.0	0	146	64	146	39	-8	3	37	10	14	2	410	81	267	107	7.7	1
	32	-3.0	0	163	56	156	35	-12	9	52	18	20	2	376	70	223	104	7.0	1
16	0	-3.6	0	181	21	239	24	-5	5	11	4	-13	3	610	75	374	61	1.9	0
	16	-2.8	0	163	52	207	55	11	5	100	15	44	14	600	108	396	76	6.3	2
	32	-2.0	0	416	59	245	64	14	7	173	35	83	21	825	170	581	107	7.9	1
17	2	78.3	34	191		959		-12		267		-10		4738		3227		44.0	
	4	16.3	14	244	34	1105	241	-6	6	265	53	-7	4	2220	485	984	357	61.2	8
	6	18.2	10	218	42	398	155	-2	4	132	33	-14	3	1161	248	628	177	37.9	9
	8	14.8	3	201	33	261	64	-11	3	145	26	-17		871	126	524	76	26.8	5
	10	7.5	3	92	17	152	25	-10	4	58	20	-14	5	653	102	438	83	23.0	4

APPENDIX B. Averages and Standard Deviations (μeq/kg litter) of Major Solutes

CODE	DAY	HYDROGEN		POTASSIUM		AMMONIUM		CHLORIDE		NITRATE		SULFATE		TOT. ACIDITY		WEAK ACIDITY		TOC (MMOL/L)	
		Avg	Std	Avg	Std	Avg	Std	Avg	Std	Avg	Std	Avg	Std	Avg	Std	Avg	Std	Avg	Std
18	2	-145.7	1	380	36	1357	86	2	3	360	175	-149	3	4485	192	3274	176	64.5	6
	4	-186.9	9	179	17	552	88	-3	5	235	48	-148	6	2091	360	1727	312	68.6	6
	6	-186.4	2	124	22	377	58	-5	4	91	17	-156	3	935	96	745	82	39.1	2
	8	-191.8		54		153		-14		37		-160		359		604		18.3	
	10	-196.0	1	73	6	180	31	-12	4	34	41	-160	2	457	80	473	79	20.7	3
19	2	-580.8	6	229		1006		1	7	275	184	-427	4	3927	862	2987	752	71.8	5
	4	-609.5	11	219	52	554	39	-9	5	32	127	-441	3	1061	154	1117	120	58.6	6
	6	-614.6	6	117	21	322	67	-13		-13	32	-435	6	602	180	894	118	33.7	4
	8	-623.9	7	89	3	177	15	-10	2	-133	38	-441	3	152	50	599	34	23.8	2
	10	-629.2	2	77	12	148	31	-11	5	-157	33	-445		10	44	491	32	16.3	4
20	2	14.9		198		713		-15		184		-1		2443		1347		11.7	
	4	8.5	4	295	61	997	310	12	8	195	158	-3	8	2101	625	1432	336	14.2	3
	6	10.9	6	170	29	646	114	-7	11	162		-9	4	1265	484	887	369	12.1	5
	8	12.4	2	95	8	532	177	3	13	304	211	-12	2	1014	361	648	189	10.6	2
	10	8.7	5	62	13	424	87	-11	2	307	84	-11	2	809	242	516	151	8.7	3
21	2	-193.5	6	357	61	1260	230	-17	2	226	51	-89	16	2221	598	1155	373	18.4	6
	4	-188.2	14	272	72	792	388	-10	2	190	51	-84	5	1531	789	927	408	13.7	4
	6	-184.1	6	220	51	611	271	-15	5	168	50	-91	5	1186	622	759	357	12.0	5
	8	-191.0	5	195	41	504	188	-12	1	163	89	-89	9	945	382	632	191	11.2	3
	10	-194.9	8	117	22	250	95	-19	0	211	90	-90	9	739	302	684	203	8.2	1
22	2	-625.9	6	347	37	977	165	-16	3	203	97	-284	15	1710	420	1359	294	15.7	4
	4	-622.1	5	269	105	647	296	-18	4	56	10	-240	10	1197	759	1172	467	9.2	
	6	-619.9	9	220	82	492	244	-11	2	68	65	-255	4	716	564	843	316	11.6	2
	8	-624.0	6	113	37	374	157	-10	1	96	82	-247	28	437	347	687	187	10.8	1
	10	-626.7	9	96	28	301	182	-19	0	44	94	-248	24	234	316	560	145	8.1	1
23	2	17.2	5	133	26	667	64	-9	8	296	62	-13	3	1626	69	942	114	14.5	4
	4	24.5	23	181	39	673	251	-2	4	113	51	-10	3	1892	514	1195	258	15.9	4
	6	38.3	18	326	24	473	46	-17		186	141	-10	2	1908	480	1397	465	11.0	3
	8	28.1	30	284	108	551	304	-9		533	54	-15	2	1661	558	1082	308	7.4	2
	10	48.8	33	701	190	657	280	-7	7	554	149	-15	0	2165	737	1459	478	7.9	5
24	2	11.8	5	187	27	733	57	-4	4	237	99	-13	3	1625	118	879	69	13.7	2
	4	1.8	2	291	25	937	37	78	15	691	276	17	6	2808	350	1868	322	21.8	5
	6	0.6	1	285	28	1792	142	165	206	833	432	18	17	3504	871	1711	994	23.2	4
	8	3.9	4	257	47	1599	96	161	45	925	272	8		2855	214	1253	176	22.3	8
	10	1.6	6	350	107	1546	240	101	21	674	190	4	7	2323	316	776	125	31.5	24
25	2	-0.5	2	236	62	243	34	-8		443	51	-15	0	987	180	744	198	8.2	1
	4	-1.4	2	174	38	397	55	-12	4	333	66	-17	2	664	241	268	249	7.2	1
	6	-2.5	1	104	18	309	116	-11		315	99	-15	2	556	133	249	113	15.3	21
	8	0.1	2	58	10	246	67	-17		215	98	-17	1	638	190	393	121	6.1	0
	10	-2.4	1	35	7	147	40	-17	1	212	33	-18	2	480	232	336	192	6.2	0
26	2	0.1	3	296	85	457	130	-7	2	564	95	-6	10	1025	96	568	39	6.7	6
	4	-0.7	3	301	95	600	222	32	16	827	164	17	7	2887	667	2288	528	17.1	2
	6	-1.3	0	214	38	351	15	52	21	1089	151	17	7	3906	1127	3557	1116	25.2	7
	8	-1.5	2	151	11	229	56	30	31	1085	100	15	5	3330	290	3102	243	17.3	7
	10	-1.2	1	146	40	400	128	10	7	790	97	-3	5	2830	837	2431	717	11.0	4

APPENDIX B. Averages and Standard Deviations (μeq/kg litter) of Major Solutes

CODE	DAY	HYDROGEN		POTASSIUM		AMMONIUM		CHLORIDE		NITRATE		SULFATE		TOT. ACIDITY		WEAK ACIDITY		TOC (MMOL/L)	
		Avg	Std	Avg	Std	Avg	Std	Avg	Std	Avg	Std	Avg	Std	Avg	Std	Avg	Std	Avg	Std
27	2	27.2	8	258	40	963	132	3	7	535	83	-3	7	2464	211	1474	188	21.5	2
	4	38.2	19	123		558		1	15	526	294	-1	18	2648	750	1762	727	28.7	20
	6	48.0	20	232	92	1108	387	10	11	360	108	-9	4	2687	925	1531	540	19.4	8
28	2	18.5	9	253	106	979	286	-6	3	433	85	-6	2	2124	486	1127	247	13.2	5
	4	27.8	8	172	12	801	41	-3	7	453	90	4	4	2092	77	1263	45	17.8	1
	6	34.0		96		432		-10		260		-1		1245		1187		13.0	
29	2	19.4	5	137	31	787	66	-6	3	242	43	-12	3	1797	245	991	185	13.0	4
	4	31.6	17	196	33	897	151	-10	5	276	113	-4	2	2475	288	1546	149	22.4	2
	6	44.2	15	200	29	723	114	-0	4	365	97	-2	2	2155	213	1388	103	19.8	2
30	2	22.1	9	189	53	903	163	4	7	424	59	-10	6	2134	365	1208	197	15.2	3
	4	24.4	5	223	17	1017	102	1	7	409	33	-5	4	2557	164	1516	82	20.7	1
	6	36.9	14	220	69	892	295	7	6	348	180	2	5	2338	621	1409	358	14.7	6
31	2	14.5	7	117	36	570	173	-8	5	190	47	-7	7	1338	344	754	172	6.7	3
	4	20.3	3	148	43	668	258	-3	8	346	78	-2	9	1752	404	1065	179	9.7	2
	6	38.3	6	182	40	805	149	-0	5	234	69	-7	4	2139	356	1296	202	17.9	2
32	2	-2.5	1	182	26	190	23	-0	4	266	38	-1	8	1046	171	858	192	8.6	5
	4	-1.2	1	232	34	159	14	-2	4	225	30	4	6	840	196	683	209	4.6	3
	6	2.0	1	253	26	228	9	-6	3	288	39	13	6	1262	79	1032	87	9.7	1
33	2	-1.6	1	203	34	237	29	-10	2	289	12	3	6	874	60	639	88	4.5	2
	4	0.7	1	282	49	215	34	-4	1	262	37	4	2	970	34	754	60	7.4	2
	6	4.0	4	241	31	226	74	-5	3	345	17	6	3	1193	106	963	149	14.1	3
34	2	0.9	1	201	36	250	35	-9	1	274	35	8	4	896	78	644	89	7.9	1
	4	0.3	2	203	26	173	30	-9	2	258	44	-1	5	914	260	741	232	6.9	3
	6	5.5	1	168	26	248	35	-7	2	318	47	3	3	1185	177	932	159	13.0	2
35	2	-1.9	1	200	35	236	17	-8	2	296	19	12	3	1079	109	846	118	12.0	2
	4	-1.3	2	167	24	296	21	-11	4	274	59	8	4	828	89	533	77	8.1	5
	6	-1.0	1	210	20	341	14	-11	4	343	30	10	8	1037	62	698	73	10.3	1
36	2	-0.5	1	160	22	129	46	-11	2	212	34	-3	5	914	133	786	118	9.9	5
	4	-1.1	1	177	31	242	33	-7	1	233	27	6	3	811	119	570	87	6.6	4
	6	1.3	1	208	25	364	31	-3	1	251	55	9	6	1405	124	1039	92	14.3	1

APPENDIX C. Cumulative Yields of Leached Major Solutes (μeq/kg litter)

CODE	DAY	H	K	NH4	Cl	NO3	SO4	TotACY	WeakACY	TOC(mM)
1	2	10.1	135	646	-7	58	7	3743	3087	18.6
	4	22.0	196	1024	-23	163	22	5119	4072	28.7
	6	29.6	274	1457	-38	370	51	7007	5520	37.8
	8	38.4	310	1752	-56	615	75	8263	6473	46.0
	10	47.9	340	2037	-76	775	94	9415	7330	53.2
	12	55.5	378	2310	-94	925	99	10465	8099	58.3
	14	81.3	412	2575	-111	1064	99	11410	8754	62.1
	16	108.1	435	2763	-127	1305	107	12196	9325	69.4
	18	133.6	454	2932	-138	1512	122	12798	9733	76.6
	20	160.2	469	3074	-151	1648	128	13532	10297	80.9
	22	179.2	481	3196	-166	1748	136	13925	10550	82.8
	24	196.5	488	3283	-185	1818	136	14195	10715	88.0
	26	204.4	498	3376	-204	1906	125	14488	10907	92.7
	28	227.8	504	3468	-224	1951	111	14843	11147	95.2
	30	233.1	509	3563	-242	2009	97	15189	11393	97.1
	32	239.2	511	3646	-260	2072	86	15514	11628	99.2
1	2	8.0	112	589	-13	43	4	3124	2527	17.7
	4	17.1	171	929	-29	146	13	4570	3623	30.2
	6	22.6	238	1214	-45	324	41	6321	5085	39.9
	8	32.5	270	1376	-63	535	56	7543	6135	49.8
	10	41.4	312	1581	-82	678	70	8588	6966	58.9
	12	47.9	342	1725	-101	805	73	9551	7778	65.7
	14	60.0	363	1889	-120	936	71	10233	8285	72.4
	16	98.0	378	2041	-137	1183	81	10777	8638	78.1
	18	128.1	386	2132	-150	1365	91	11275	9015	83.4
	20	164.2	393	2233	-165	1525	104	11856	9459	88.5
	22	179.4	399	2301	-181	1651	108	12266	9786	92.1
	24	188.3	403	2366	-202	1719	101	12483	9929	95.9
	26	192.1	405	2438	-221	1808	86	12711	10081	98.6
	28	207.3	407	2499	-241	1846	70	12969	10264	101.5
	30	207.7	409	2571	-259	1898	56	13228	10449	104.7
	32	213.6	410	2611	-277	1954	46	13486	10662	107.7
1	2	9.9	89	543	-14	31	-2	2903	2350	24.5
	4	17.9	169	828	-32	125	6	4237	3391	36.5
	6	23.8	236	1199	-48	292	25	5875	4652	44.3
	8	31.3	287	1450	-67	457	33	6969	5488	53.4
	10	39.1	317	1712	-88	588	40	7931	6180	61.8
	12	44.5	340	1921	-107	688	41	8812	6847	67.6
	14	64.6	371	2052	-127	808	36	9614	7497	72.8
	16	95.0	390	2214	-145	1009	38	10199	7891	77.7
	18	115.9	409	2329	-160	1167	45	10615	8170	82.1
	20	138.7	420	2445	-177	1322	48	11102	8518	86.3
	22	150.1	426	2540	-195	1467	48	11410	8719	89.9
	24	163.8	431	2616	-212	1524	44	11647	8867	95.0
	26	169.1	437	2696	-232	1587	31	11902	9036	100.7
	28	187.5	441	2778	-252	1632	19	12234	9269	106.2
	30	187.5	445	2861	-271	1676	4	12519	9470	108.3
	32	191.3	447	2909	-290	1742	-10	12797	9696	112.5

APPENDIX C. Cumulative Yields of Leached Major Solutes (μeq/kg litter)

CODE	DAY	H	K	NH4	Cl	NO3	SO4	TotACY	WeakACY	TOC(mM)
2	4	22.5	230	920	-3	55	17	3811	2870	35.7
	8	49.4	325	1391	-12	169	44	5235	3794	46.7
	12	109.6	405	1727	-23	372	74	6243	4407	55.9
	16	162.8	448	1885	-35	588	102	6747	4699	60.8
	20	192.7	486	1976	-50	771	118	7119	4951	64.8
	24	219.1	517	2065	-66	891	128	7530	5245	68.2
	28	257.1	536	2157	-82	970	129	7984	5570	73.5
	32	306.5	549	2272	-99	1070	128	8478	5899	76.4
2	4	35.2	203	980	-3	70	39	3751	2735	15.2
	8	65.7	283	1668	-13	226	73	5624	3890	23.2
	12	134.3	327	2073	-26	481	115	6840	4633	27.9
	16	197.0	357	2286	-40	779	147	7372	4889	32.9
	20	231.2	382	2413	-57	1040	168	7798	5153	36.3
	24	263.7	409	2552	-74	1203	180	8206	5391	40.3
	28	309.7	418	2696	-92	1287	185	8636	5630	43.5
	32	362.9	426	2848	-110	1410	201	9090	5879	47.1
2	4	26.0	171	1047	-9	66	20	4921	3848	44.7
	8	61.8	236	1649	-23	243	58	7000	5289	64.4
	12	142.7	283	2025	-37	469	113	8457	6289	75.8
	16	221.2	317	2208	-52	724	152	9052	6623	82.8
	20	259.7	352	2314	-67	931	180	9502	6928	90.4
	24	307.2	374	2428	-86	1096	197	10000	7264	97.3
	28	360.1	397	2552	-103	1220	209	10501	7590	103.7
	32	422.8	410	2677	-120	1356	229	11132	8032	107.9
3	8	66.5	353	1904	1	222	36	6363	4393	25.8
	16	249.9	469	2540	-6	498	88	8265	5475	36.7
	24	392.7	545	2994	-17	665	109	9266	5879	46.7
	32	543.2	648	3500	-25	866	133	10306	6263	50.2
3	8	79.8	329	1615	3	181	50	7239	5544	24.3
	16	228.4	433	2246	-2	426	122	9245	6771	37.1
	24	329.1	498	2635	-10	571	176	10336	7372	42.4
	32	472.7	578	3107	-18	748	242	11396	7817	46.4
3	8	58.9	310	1492	0	162	40	6046	4495	31.3
	16	188.1	386	2031	-8	388	102	7889	5670	43.7
	24	275.1	439	2407	-22	522	135	8738	6056	53.4
	32	374.3	502	2822	-31	686	169	9437	6242	57.9
4	16	130.5	399	2614	4	295	68	6426	3681	16.7
	32	356.6	809	4370	10	754	148	9116	4390	23.9
4	16	101.8	353	2831	12	274	106	6984	4052	8.4
	32	219.6	699	4744	39	673	239	9935	4971	13.5
4	16	79.4	593	2956	11	241	82	8860	5824	11.2
	32	189.6	1028	4845	22	597	177	12396	7361	32.7

APPENDIX C. Cumulative Yields of Leached Major Solutes (μeq/kg litter)

CODE	DAY	H	K	NH4	Cl	NO3	SO4	TotACY	WeakACY	TOC(mM)
5	2	1.0	78	268	-2	25	9	999	731	4.0
	4	0.0	122	483	3	79	25	1628	1146	15.0
	6	-2.5	139	612	-10	102	36	2100	1490	20.1
	8	-5.5	154	716	-29	119	35	2443	1733	23.8
	10	-7.0	163	828	-48	137	33	2945	2124	28.3
	12	-10.3	175	1009	-67	178	32	3365	2366	31.7
	14	-13.7	182	1159	-84	181	25	3718	2573	36.3
	16	-14.4	201	1410	-97	171	26	4290	2895	39.5
	18	-17.7	205	1594	-112	222	29	4665	3088	43.9
	20	-20.1	213	1788	-131	282	22	5052	3284	45.8
	22	-23.2	222	1974	-149	334	16	5445	3494	47.7
	24	-25.8	230	2138	-165	428	4	5848	3737	53.0
	26	-29.3	236	2257	-184	457	-6	6179	3951	59.9
	28	-31.9	239	2362	-203	464	-17	6591	4261	64.4
	30	-34.4	245	2512	-223	472	-28	6996	4518	67.5
	32	-37.1	249	2630	-243	484	-37	7406	4814	69.9
5	2	1.7	124	441	-5	19	6	1911	1469	3.6
	4	1.0	215	794	-3	60	29	2949	2154	13.7
	6	-0.8	260	1036	-17	97	48	3817	2782	18.6
	8	-3.6	295	1220	-35	124	61	4465	3249	23.9
	10	-4.0	323	1442	-55	134	65	5246	3808	29.5
	12	-7.0	348	1562	-74	181	55	5938	4383	37.1
	14	-10.5	363	1653	-92	189	42	6376	4734	41.6
	16	-10.8	390	1843	-105	203	34	7110	5278	46.2
	18	-14.2	399	1932	-120	283	30	7516	5598	53.2
	20	-17.1	407	2033	-139	312	20	7961	5945	57.4
	22	-20.0	412	2105	-158	361	7	8398	6313	61.4
	24	-22.8	420	2185	-174	448	-4	8852	6690	65.4
	26	-26.0	428	2261	-193	461	-16	9272	7037	69.5
	28	-27.7	431	2337	-213	461	-28	9730	7421	72.6
	30	-30.2	439	2432	-233	462	-40	10199	7797	76.2
	32	-33.1	441	2519	-253	472	-51	10707	8220	79.6
5	2	1.3	106	334	-11	8	2	1512	1177	5.5
	4	-0.9	182	587	-15	38	13	2388	1802	18.0
	6	-3.0	211	764	-30	53	37	3061	2300	25.7
	8	-6.1	236	908	-49	67	56	3471	2569	31.5
	10	-7.0	260	1064	-68	73	64	4087	3030	38.9
	12	-10.5	276	1203	-89	70	61	4640	3448	43.7
	14	-13.9	293	1321	-109	71	52	5136	3829	50.7
	16	-16.2	327	1547	-126	56	52	6012	4481	57.2
	18	-19.6	342	1666	-144	91	63	6576	4929	66.7
	20	-22.0	355	1805	-163	110	62	7163	5380	71.1
	22	-24.9	365	1951	-182	149	57	7763	5837	77.5
	24	-27.7	372	2084	-201	211	49	8349	6292	85.9
	26	-31.0	376	2191	-221	215	33	8886	6727	92.7
	28	-32.9	382	2272	-241	209	17	9453	7213	99.6
	30	-35.9	388	2386	-262	205	2	9907	7556	102.8
	32	-38.8	390	2495	-283	211	-13	10385	7929	107.7

APPENDIX C. Cumulative Yields of Leached Major Solutes (μeq/kg litter)

CODE	DAY	H	K	NH4	Cl	NO3	SO4	TotACY	WeakACY	TOC(mM)
6	4	-1.5	124	198	-11	33	21	876	680	4.8
	8	-3.8	203	382	-21	78	36	1568	1189	10.1
	12	-6.1	310	562	-32	119	44	2206	1650	16.0
	16	0.6	454	872	-49	169	55	3281	2409	22.8
	20	-1.9	553	1096	-67	204	62	4214	3120	29.8
	24	-1.5	631	1284	-85	233	55	5005	3722	40.5
	28	-1.3	701	1499	-103	249	47	5833	4335	48.5
	32	-1.3	783	1685	-121	273	39	6595	4911	52.6
6	4	-2.1	51	169	-6	43	40	718	551	4.8
	8	-4.0	110	323	-13	99	65	1319	1000	9.9
	12	-6.1	201	473	-22	150	85	1900	1433	16.0
	16	-4.2	283	680	-40	208	98	2804	2128	20.9
	20	-6.6	333	840	-59	254	108	3509	2676	28.7
	24	-8.2	371	950	-76	294	100	4072	3130	34.6
	28	-10.1	409	1108	-94	322	92	4720	3622	39.7
	32	-11.6	458	1235	-111	353	86	5311	4087	44.7
6	4	-2.3	87	186	-15	25	27	589	405	6.3
	8	-5.1	160	350	-31	70	31	1150	805	14.3
	12	-8.0	258	509	-47	100	32	1697	1195	22.6
	16	-8.0	369	790	-66	139	36	2470	1688	33.4
	20	-9.9	431	977	-85	159	38	3089	2123	47.5
	24	-11.0	481	1112	-104	168	27	3583	2483	62.1
	28	-12.2	526	1286	-122	169	17	4159	2885	73.0
	32	-13.5	583	1435	-139	173	8	4712	3291	79.4
7	8	0.2	53	241	-5	42	28	616	374	5.9
	16	5.5	137	551	-18	81	44	1340	783	16.5
	24	6.5	211	910	-33	106	41	2267	1350	30.0
	32	7.0	279	1307	-49	135	33	3184	1870	38.9
7	8	3.4	114	285	-7	62	25	1191	903	5.5
	16	18.6	230	635	-16	107	48	2495	1841	12.5
	24	24.5	338	1032	-30	140	47	3836	2780	23.0
	32	27.7	428	1461	-44	176	46	5092	3603	30.6
7	8	1.0	95	380	-10	31	6	963	582	8.5
	16	11.0	198	804	-24	54	8	2122	1308	20.7
	24	13.9	283	1256	-39	67	3	3325	2055	37.1
	32	15.2	353	1733	-54	83	-3	4457	2709	48.3
8	16	2.3	82	555	-10	60	25	1265	708	12.0
	32	4.4	209	1389	-10	135	76	2749	1356	26.4
8	16	3.2	124	384	-1	53	30	1089	702	9.7
	32	6.3	268	1007	1	115	76	2461	1447	21.5
8	16	5.9	63	481	-6	46	21	1482	995	17.9
	32	11.0	150	1298	-8	96	74	3186	1878	37.8

APPENDIX C. Cumulative Yields of Leached Major Solutes (μeq/kg litter)

CODE	DAY	H	K	NH4	Cl	NO3	SO4	TotACY	WeakACY	TOC(mM)
9	2	0.8	272	331	10	23	17	688	356	8.2
	4	-0.2	526	559	12	101	42	1338	779	18.2
	6	-3.4	817	792	10	257	94	2029	1240	30.0
	8	-6.1	1058	1015	3	540	117	2563	1555	42.9
	10	-7.8	1191	1142	-7	983	174	2934	1799	48.6
	12	-10.8	1321	1248	-21	1458	196	3295	2057	54.2
	14	-13.3	1461	1359	-37	1561	199	3732	2386	57.6
	16	-14.3	1609	1454	-54	1830	192	4062	2623	62.1
	18	-16.7	1754	1604				4357	2770	67.1
	20	-19.2	1866	1729				4600	2890	73.3
	22	-16.7	1951	1828				4799	2988	77.3
	24	-19.4	2054	1961				5071	3130	84.6
	26	-21.3	2164	2107				5345	3259	90.1
	28	-23.2	2274	2257				5675	3441	96.9
	30	-25.1	2366	2440				6017	3603	101.5
	32	-27.2	2459	2601				6312	3738	106.8
9	2	-0.4	226	334	8	20	19	572	238	10.3
	4	-3.0	422	652	14	82	51	965	317	22.6
	6	-6.3	675	973	10	246	106	1530	563	31.7
	8	-8.7	876	1252	2	556	133	2024	780	40.5
	10	-10.6	999	1400	-11	915	199	2339	949	49.6
	12	-13.3	1093	1530	-26	1293	222	2647	1131	57.6
	14	-16.3	1222	1666	-42	1373	221	3032	1382	63.5
	16	-18.1	1309	1796	-60	1573	213	3264	1487	70.5
	18	-20.9	1381	1875	-78	1803	204	3521	1666	77.5
	20	-23.6	1459	1957	-96	1972	192	3728	1794	84.0
	22	-21.8	1518	2029	-115	2097	183	3927	1920	90.8
	24	-24.9	1606	2155	-135	2189	167	4222	2092	97.9
	26	-27.2	1683	2278	-156	2211	151	4509	2258	103.0
	28	-29.3	1786	2417	-176	2237	137	4799	2412	108.5
	30	-32.1	1854	2563	-196	2277	130	5010	2479	114.2
	32	-34.0	1887	2687	-217	2307	116	5252	2599	120.1
9	2	-0.4	203	435	1	13	13	713	278	10.6
	4	-2.3	374	768	0	65	32	1328	563	20.5
	6	-5.5	566	1119	-6	198	77	1987	874	32.9
	8	-8.9	745	1412	-16	449	94	2590	1187	
	10	-11.4	884	1575	-31	782	146	3021	1457	
	12	-14.8	1026	1733	-48	1133	164	3414	1696	
	14	-18.4	1195	1902	-66	1206	159	3937	2053	
	16	-20.3	1332	2048	-85	1369	148	4292	2264	
	18	-22.4	1452	2149				4602	2475	
	20	-24.7	1547	2257				4870	2637	
	22	-21.8	1625	2348				5100	2773	
	24	-24.7	1720	2451				5419	2993	
	26	-27.4	1805	2567				5749	3210	
	28	-28.5	1917	2694				6103	3437	
	30	-29.5	2020	2833				6456	3653	
	32	-31.5	2122	2947				6764	3849	

APPENDIX C. Cumulative Yields of Leached Major Solutes (μeq/kg litter)

CODE	DAY	H	K	NH4	Cl	NO3	SO4	TotACY	WeakACY	TOC(mM)
10	4	-3.8	376	777	23	42	42	1568	794	15.6
	8	-6.8	684	1351	26	178	104	2632	1287	28.1
	12	-8.7	984	2024	18	442	162	3849	1835	35.3
	16	-11.8	1216	2333	11	799	196	4450	2128	43.5
	20	-14.0	1450	2656	3	947	208	5187	2545	50.2
	24	-15.4	1607	2818	-9	1037	228	5580	2778	60.2
	28	-18.4	1758	2987	-20	1119	233	6017	3049	72.2
	32	-21.5	1921	3133	-29	1246	247	6445	3333	79.4
10	4	-3.2	426	625	10	32	32	1514	892	13.3
	8	-5.7	754	1106	12	147	96	2398	1298	26.0
	12	-7.4	1150	1653	12	442	163	3625	1980	37.6
	16	-10.5	1419	1898	6	881	218	4197	2309	44.8
	20	-13.3	1712	2202	0	1118	235	4883	2694	53.2
	24	-15.8	1982	2347	-13	1244	241	5250	2919	62.9
	28	-19.2	2191	2485	-30	1305	237	5603	3137	73.1
	32	-22.2	2405	2616	-42	1410	237	6021	3427	83.4
10	4	-3.4	475	747	3	16	25	1113	370	16.0
	8	-7.0	836	1277	1	95	61	1936	666	29.3
	12	-8.9	1212	1900	1	432	135	3116	1225	39.7
	16	-11.6	1469	2200	-4	937	199	3574	1385	48.6
	20	-13.9	1729	2480	-8	1201	246	4237	1771	59.1
	24	-15.2	1974	2609	-20	1370	262	4537	1944	72.0
	28	-18.4	2185	2734	-37	1421	264	4864	2148	87.2
	32	-21.8	2411	2833	-53	1518	275	5198	2387	99.2
11	8	-1.5	361	395	11	82	87	1151	758	23.0
	16	-3.2	591	692	11	551	184	1837	1149	36.7
	24	-6.6	779	846	8	678	228	2263	1424	50.4
	32	-9.5	939	973	8	880	280	2620	1657	61.4
11	8	-1.1	321	450	17	115	58	1083	634	15.0
	16	-2.9	526	798	21	545	137	1740	945	27.5
	24	-6.1	692	969	12	717	153	2126	1163	41.0
	32	-8.9	821	1115	2	953	195	2449	1343	53.8
11	8	-3.0	224	500	24	136	51	1220	723	28.9
	16	-5.3	410	859	36	440	106	2020	1166	43.9
	24	-8.5	547	1058	30	528	113	2497	1447	58.9
	32	-12.0	671	1235	25	689	136	2939	1716	72.6
12	16	1.9	606	838	23	464	89	1569	730	19.2
	32	3.8	836	1216	51	1051	253	2333	1113	36.9
12	16	2.9	673	737	5	431	124	1731	991	27.0
	32	4.6	880	1087	13	895	310	2531	1439	46.2
12	16	-0.2	545	627	17	450	74	1465	838	20.3
	32	2.1	730	914	35	956	215	2044	1128	41.6

CODE	DAY	H	K	NH4	Cl	NO3	SO4	TotACY	WeakACY	TOC(mM)
13	2	-3.2	116	224	9	29	4	496	275	8.2
	4	-6.3	234	439	13	65	1	1129	696	16.9
	6	-9.5	382	625	8	99	3	1606	990	26.8
	8	-12.4	534	821	-1	180	2	2155	1346	32.7
	10	-15.4	618	931	-17	276	-7	2489	1573	36.7
	12	-18.4	690	1022	-34	365	-10	2770	1766	39.9
	14	-22.0	751	1062	-45	422	-9	3010	1970	42.4
	16	-25.7	794	1096	-64	493	-23	3177	2106	45.2
	18	-29.1	847	1129	-82	506	-36	3350	2250	48.6
	20	-32.5	885	1165	-101	511	-51	3532	2400	50.5
	22	-36.1	925	1214	-121	512	-69	3705	2527	53.4
	24	-39.3	963	1260	-137	509	-86	3868	2648	56.4
	26	-42.6	1003	1307	-156	507	-102	4041	2777	60.2
	28	-45.8	1058	1359	-177	508	-118	4256	2943	63.5
	30	-48.8	1113	1412	-196	515	-131	4486	3123	66.3
	32	-52.1	1180	1467	-216	509	-149	4649	3235	70.1
13	2	-3.2	226	281	18	22	11	331	53	4.8
	4	-6.1	422	543	18	50	14	703	166	9.3
	6	-9.1	559	771	8	74	24	1066	304	12.5
	8	-12.0	718	1024	1	123	29	1435	422	15.6
	10	-15.4	819	1144	-12	199	29	1588	460	19.0
	12	-18.6	887	1254	-29	260	29	1733	497	22.0
	14	-21.8	941	1336	-38	310	24	1839	525	24.1
	16	-25.3	990	1402	-56	372	9	1913	536	27.4
	18	-28.5	1053	1465	-73	389	-7	2058	621	30.6
	20	-31.9	1100	1526	-91	397	-24	2155	661	32.9
	22	-35.3	1148	1594	-110	403	-42	2261	702	36.9
	24	-38.8	1201	1668	-126	404	-59	2386	757	40.1
	26	-42.0	1250	1748	-147	402	-78	2493	787	43.7
	28	-45.0	1309	1843	-167	404	-94	2603	805	46.4
	30	-48.3	1372	1961	-187	414	-110	2732	820	49.2
	32	-51.7	1435	2090	-207	416	-128	2869	831	53.0
13	2	-3.6	262	162	12	15	16	353	196	9.9
	4	-7.2	496	306	12	34	23	751	452	21.7
	6	-10.6	701	439	2	54	33	1091	662	33.4
	8	-14.1	954	612	-11	91	43	1518	920	40.5
	10	-17.3	1112	695	-28	145	52	1748	1070	47.5
	12	-20.7	1250	768	-47	193	54	1927	1180	53.4
	14	-24.1	1341	817	-61	232	55	2071	1278	57.9
	16	-27.7	1442	859	-82	276	43	2206	1375	64.4
	18	-31.2	1549	901	-101	273	31	2436	1566	69.4
	20	-34.6	1663	946	-121	267	16	2590	1678	73.7
	22	-38.2	1782	1005	-143	261	-1	2715	1748	78.9
	24	-41.4	1902	1062	-161	254	-17	2888	1867	84.9
	26	-44.7	2020	1123	-183	248	-32	3070	1992	91.8
	28	-47.9	2145	1188	-204	248	-47	3241	2102	97.1
	30	-51.1	2284	1256	-227	246	-64	3424	2219	101.6
	32	-54.5	2400	1328	-250	245	-79	3597	2323	107.2

APPENDIX C. Cumulative Yields of Leached Major Solutes (μeq/kg litter)

CODE	DAY	H	K	NH4	Cl	NO3	SO4	TotACY	WeakACY	TOC(mM)
14	4	-3.4	264	682	24	44	42	1104	425	12.2
	8	-4.8	507	1250	25	106	65	2160	915	19.0
	12	-7.0	665	1693	21	189	88	2666	980	25.7
	16	-9.7	870	2158	14	257	110	3152	1003	29.1
	20	-12.5	1056	2531	3	296	107	3734	1215	34.0
	24	-15.0	1214	2746	-10	327	106	4125	1394	40.3
	28	-17.1	1362	2951	-23	327	90	4526	1592	46.4
	32	-18.8	1488	3131	-39	333	99	4904	1792	52.1
14	4	-3.6	433	409	14	57	51	912	507	7.4
	8	-4.6	771	652	13	130	89	1702	1055	14.4
	12	-7.4	1043	872	8	220	135	2056	1191	19.8
	16	-10.3	1353	1113	-2	302	166	2447	1344	25.3
	20	-12.7	1672	1341	-17	348	168	2972	1643	30.6
	24	-15.4	1944	1452	-35	386	163	3354	1917	36.7
	28	-18.1	2187	1592	-51	391	150	3745	2171	41.2
	32	-20.1	2423	1702	-59	413	185	4051	2369	46.0
14	4	-3.4	243	500	4	23	62	1609	1113	12.4
	8	-6.1	505	800	0	75	104	3008	2214	20.5
	12	-9.1	692	1045	-8	142	152	3979	2943	29.3
	16	-12.0	969	1302	-16	200	189	5111	3821	36.3
	20	-15.0	1193	1573	-30	230	194	5920	4362	44.1
	24	-17.9	1368	1739	-43	256	192	6435	4715	52.4
	28	-20.5	1507	1900	-58	254	178	6988	5109	60.4
	32	-22.8	1659	2037	-70	261	193	7427	5413	67.6
15	8	-3.2	365	319	0	60	27	553	237	7.2
	16	-6.5	637	578	-8	116	51	1020	449	13.3
	24	-9.5	855	766	-15	160	67	1355	599	21.1
	32	-12.5	1079	956	-22	224	88	1670	727	27.4
15	8	-3.4	247	435	4	88	36	686	254	6.5
	16	-6.3	414	657	-2	157	74	1258	607	11.4
	24	-9.1	540	768	-9	197	87	1659	900	18.1
	32	-12.4	692	925	-16	258	105	2020	1107	24.5
15	8	-2.9	220	363	6	101	63	619	259	9.5
	16	-5.9	369	549	2	181	97	1210	667	18.1
	24	-8.9	464	690	-10	206	112	1706	1025	26.6
	32	-11.8	578	809	-32	238	134	2158	1361	34.8
16	16	-2.9	120	165	15	100	31	477	314	5.3
	32	-5.1	488	355	35	275	91	1134	784	12.7
16	16	-2.5	220	270	12	115	43	676	409	5.5
	32	-4.0	703	585	26	322	132	1674	1093	12.4
16	16	-3.0	150	186	5	86	59	648	465	8.2
	32	-5.1	547	416	12	222	159	1467	1056	17.7

APPENDIX C. Cumulative Yields of Leached Major Solutes (μeq/kg litter)

CODE	DAY	H	K	NH4	Cl	NO3	SO4	TotACY	WeakACY	TOC(mM)
17	2	114.0								
	4	145.2								
	6	159.6								
	8	172.7								
	10	183.7								
17	2	75.4	310	1345	-4	348	-3	5132	3711	69.0
	4	89.9	593	2633	-12	564	-10	7794	5071	137.9
	6	119.1	859	3198	-13	709	-27	9097	5780	182.6
	8	137.0	1075	3528	-21	828	-46	9992	6327	209.4
	10	142.9	1188	3692	-26	903	-63	10678	6843	236.7
17	2	45.6	266	1554	-9	475	-5	4343	2744	63.1
	4	48.8	490	2386	-20	732	-8	6122	3687	116.7
	6	59.7	692	2645	-26	827	-22	7140	4436	157.7
	8	73.1	916	2892	-41	971		7988	5023	189.4
	10	78.7	1001	3061	-55	1034		8607	5467	212.6
18	2	-144.6	416	1269	0	559	-149	4311	3186	57.8
	4	-324.3	576	1851	-6	834	-303	6171	4645	119.3
	6	-510.2	722	2172	-7	941	-457	7005	5344	156.4
	8									
	10									
18	2	-146.5	344	1440	-1	296	-147	4454	3160	68.6
	4	-330.4	538	2062	2	543	-289	6960	5229	141.9
	6	-518.7	640	2434	-5	616	-448	7984	6069	183.3
	8	-709.8	718	2670	-9	707	-605	8685	6725	212.4
	10	-906.1	787	2856	-17	728	-763	9234	7284	237.1
18	2	-145.9	380	1360	5	226	-153	4691	3477	67.3
	4	-343.0	562	1813	0	409	-300	6599	5129	138.1
	6	-528.0	684	2250	-6	504	-456	7547	5825	176.9
	8	-720.5	773	2497	-21	610	-615	8153	6377	202.7
	10	-917.5	846	2643	-33	610	-777	8560	6834	221.0
19	2	-581.4			3	485	-424	3135	2196	67.1
	4	-1203.8			-10	374	-868	4142	3263	121.2
	6	-1818.3			-20	388	-1304	4883	4254	158.5
	8	-2448.9			-28	298	-1745	5016	4835	181.6
	10	-3080.1			-36	105	-2189	5016	5295	198.0
19	2	-574.0	380	1725	7	141	-432	4845	3694	71.8
	4	-1179.5	606	2312	-3	276	-871	6080	4947	136.8
	6	-1799.7	739	2670	-8	272	-1300	6745	5875	171.0
	8	-2416.8	827	2858	-19	120	-1744	6954	6513	196.5
	10	-3043.8	914	3017	-35	-10		7011	7038	216.8
19	2	-586.9	310	1315	-6	200	-426	3800	3072	76.6
	4	-1187.5	473	1826	-10	272	-865	4741	4102	133.2
	6	-1796.6	566	2071		222	-1305	5140	4865	162.8
	8	-2420.6	659	2231		65	-1742	5254	5444	185.4
	10	-3050.1	724	2343		-84	-2184	5225	5932	197.6

APPENDIX C. Cumulative Yields of Leached Major Solutes (μeq/kg litter)

CODE	DAY	H	K	NH4	Cl	NO3	SO4	TotACY	WeakACY	TOC(mM)
20	2	11.0	302	1163	-12	230	10	2538	1365	19.6
	4	23.0	547	1946	-7	443	1	4412	2443	30.8
	6	38.0	711	2504	-2	648	-12	5639	3097	39.7
	8	48.1	806	2882	-14	817	-27	6468	3537	48.6
	10	51.3	857	3251	-26	1100	-39	7258	3956	55.5
20	2	18.8	296	999	-12	344	10	2348	1330	15.4
	4	23.8	574	1854	-1	688	3	4678	2800	29.1
	6	28.1	718	2459	-14	990	-6	5981	3494	39.0
	8	40.1	806	2951	-4	1186	-18	7180	4189	49.8
	10	50.7	865	3329	-16	1423	-28	8009	4629	57.4
20	2									
	4									
	6									
	8									
	10									
21	2	-189.6	308	1104	-18	200	-105	1727	813	13.7
	4	-378.3	505	1501	-26	374	-188	2466	1343	24.5
	6	-562.2	688	1938	-35	486	-276	3215	1839	33.8
	8	-758.3	851	2316	-46	566	-362	3916	2358	42.9
	10	-961.8	954	2500	-65	813	-448	4427	2888	51.3
21	2	-200.6	336	1151	-18	194	-89	2050	1099	16.7
	4	-374.3	614	1959	-27	342	-178	3587	2003	28.1
	6	-552.5	813	2432	-42	524	-267	4497	2618	37.2
	8	-741.9	994	2844	-55	781	-348	5246	3144	46.6
	10	-930.8	1100	3051	-74	889	-433	5871	3750	54.0
21	2	-190.2	426	1524	-14	285	-72	2886	1552	24.9
	4	-392.3	768	2696	-27	532	-151	5202	2898	43.7
	6	-582.5	1045	3620	-46	741	-248	7100	4063	61.4
	8	-769.9	1286	4340	-58	893	-348	8485	4916	76.6
	10	-962.2	1429	4699	-78	1170	-449	9567	5830	85.3
22	2	-626.2	380	1157	-15	219	-278	2033	1502	18.6
	4	-1254.0	739	2062	-28	264	-526	3914	3107	34.6
	6	-1863.5	994	2782	-38	281	-781	5111	4193	48.5
	8	-2483.9	1148	3336	-48	456	-1050	5947	5094	60.4
	10	-3100.4	1275	3848	-67	599	-1322	6517	5770	69.7
22	2	-631.4	353	941	-15	291	-301	1862	1553	16.7
	4	-1250.8	646	1655	-35	348	-531	3192	2788	28.3
	6	-1874.2	925	2176	-45	393	-782	4047	3746	38.8
	8	-2505.0	1007	2470	-54	494	-1039	4313	4348	49.2
	10	-3139.0	1081	2651	-73	528	-1286	4256	4744	56.6
22	2	-620.0	308	834	-19	99	-274	1235	1021	11.8
	4	-1239.0	462	1157	-39	163	-515	1615	1697	
	6	-1865.8	589	1393	-52	304	-773	1710	2183	
	8	-2486.7	692	1664	-63	315	-988	1919	2741	
	10	-3116.2	779	1877	-82	272	-1212	2109	3348	

APPENDIX C. Cumulative Yields of Leached Major Solutes (μeq/kg litter)

CODE	DAY	H	K	NH4	Cl	NO3	SO4	TotACY	WeakACY	TOC(mM)
23	2	22.2	145	673	-14	306	-16	1550	856	14.0
	4	72.2	371	1560	-14	407	-25	3804	2172	30.2
	6	130.2	682	1986	-19	433	-36	5915	3799	42.0
	8	190.2	1055	2770		1027	-50	7750	4790	50.3
	10	277.6	1756	3209		1519	-65	9434	5947	58.5
23	2	11.4	103	600	0	230	-11	1683	1072	18.6
	4	18.2	257	998	-7	399	-24	2987	1971	38.2
	6	53.0	570	1514		644	-32	5240	3673	52.1
	8	76.8	886	2176		1155	-49	7351	5099	61.0
	10	105.3	1397	2736		1600	-64	9149	6307	73.9
23	2	17.9	151	728	-12	353	-11	1645	900	11.0
	4	34.6	314	1461	-12	423	-19	3766	2270	23.0
	6	56.6	667	1938		709	-30	5126	3132	30.2
	8	57.2	831	2145		1203	-46	6164	3961	35.3
	10	87.6	1722	3118		1927	-61	9177	5972	37.8
24	2	17.1	217	787	-5	336	-11	1759	956	11.3
	4	19.2	479	1718	58	1216	3	4298	2561	27.1
	6	20.9	762	3540	98	2128	7	7121	3561	45.3
	8	23.8	994	5121	311	3293	40	9755	4610	58.9
	10	31.7	1235	6933	435	4184	51	12369	5404	71.0
24	2	7.4	165	673	0	138	-11	1541	861	13.9
	4	11.2	465	1577	77	957	3	4222	2634	39.1
	6	10.5	723	3494	130	1324	17	7425	3921	64.4
	8	18.6	951	5197	264	1952	30	10486	5271	90.3
	10	16.9	1407	6544	349	2492	32	12474	5913	114.2
24	2	10.8	181	741	-7	238	-16	1573	821	15.8
	4	10.5	491	1718	86	612	8	4777	3049	40.1
	6	11.4	804	3355	489	1832	44	9263	5896	66.3
	8	12.0	1116	4868	625	2812		12133	7254	93.9
	10	10.5	1469	6346	718	3403		14501	8144	152.2
25	2	0.8	205	217	4	498	-16	1189	972	9.2
	4	1.3	369	587	-10	895	-32	2113	1524	16.5
	6	-1.7	492	998	-15	1298	-48	2656	1660	16.5
	8	1.1	561	1309	-29	1623	-64	3485	2174	22.4
	10	-0.4	604	1497	-47	1870	-79	4218	2721	28.6
25	2	0.4	196	281	-6	397	-15	923	642	7.6
	4	-1.9	338	642	-13	732	-34	1372	732	14.1
	6	-3.0	439	977		1066	-51	2067	1094	20.3
	8	-4.7	488	1155		1203	-70	2516	1365	26.6
	10	-8.0	522	1300		1385	-89	2945	1653	32.9
25	2	-2.7	308	232		435	-15	847	618	7.8
	4	-5.1	524	692		701	-32	1467	780	15.6
	6	-8.4	612	874		908	-45	1896	1031	55.1
	8	-9.3	669	1121		1093	-62	2535	1423	61.4
	10	-11.8	698	1229		1300	-81	2812	1594	67.5

APPENDIX C. Cumulative Yields of Leached Major Solutes (μeq/kg litter)

CODE	DAY	H	K	NH4	Cl	NO3	SO4	TotACY	WeakACY	TOC(mM)
26	2	3.8	226	562	-5	589	-2	1113	547	7.7
	4	6.8	551	1321	17	1362	17	3937	2609	22.8
	6	5.5	722	1655	57	2487	26	7330	5670	41.3
	8	6.1	885	1948	108	3652	40	10914	8960	52.2
	10	5.7	1003	2288	114	4385	40	13091	10798	59.3
26	2	-2.3	272	496	-9	460	0	1037	544	12.5
	4	-5.1	654	1191	42	1157	22	4621	3435	30.4
	6	-6.5	880	1545	117	2081	41	7748	6210	62.3
	8	-9.1	1022	1752	160	3198	62	11142	9399	87.6
	10	-9.7	1214	2299	179	4100	53	14915	12626	102.4
26	2	-1.3	391	312	-7	644	-17	923	613	0.0
	4	-3.6	587	657	16	1655	-9	3177	2523	18.2
	6	-4.9	832	1022	55	2875	14	8375	7358	43.5
	8	-7.2	980	1210	50	3848	25	11389	10186	59.3
	10	-9.9	1107	1524	56	4583	25	13927	12413	70.3
27	2	33.8	258	1087	-4	555	-3	2451	1330	19.8
	4	94.2			14	1419	17	5960	3932	72.0
	6	164.0			36	1847	11	9565	5929	98.0
27	2	29.6	219	825	9	445	3	2259	1405	20.5
	4	57.9	445	1759	3	823	-7	4549	2731	38.0
	6	88.2	608	2546	2	1058	-20	6304	3670	48.5
27	2	18.1	298	977	3	606	-10	2681	1686	24.3
	4	43.9	445	1739	-7	941	-22	4826	3044	40.7
	6	88.0	642	2740	4	1357	-29	7528	4700	62.5
28	2	29.3	264	941	-3	397	-6	1866	896	8.0
	4	66.7	447	1746	1	836	2	4022	2210	27.0
	6									
28	2	14.4	353	1283	-6	530	-4	2685	1388	15.4
	4	36.1	513	2041	-12	901	-2	4691	2614	32.3
	6	69.7	640	2728	-13	1284	15	6561	3763	53.2
28	2	11.8	143	714	-8	372	-9	1822	1096	16.2
	4	36.1	317	1554	-17	922	-7	3935	2345	33.6
	6	70.5	481	2185	-23	1341	-6	5825	3570	51.9
29	2	23.9	146	726	-3	291	-15	1598	848	10.5
	4	74.1	348	1630	-7	688	-22	4205	2500	34.2
	6	134.1	549	2449	-3	1151	-21	6506	3922	55.3
29	2	13.9	163	857	-8	213	-10	2071	1200	17.7
	4	32.1	390	1902	-23	388	-14	4744	2810	40.9
	6	62.3	618	2656	-27	657	-17	6998	4279	61.2
29	2	20.3	103	777	-6	222	-10	1721	924	10.8
	4	46.7	264	1520	-18	477	-13	3867	2300	31.2
	6	89.1	435	2117	-19	840	-15	5778	3572	49.0

APPENDIX C. Cumulative Yields of Leached Major Solutes (μeq/kg litter)

CODE	DAY	H	K	NH4	Cl	NO3	SO4	TotACY	WeakACY	TOC(mM)
30	2	25.1	201	904	3	443	-16	2079	1149	14.6
	4	53.0	433	2027	13	878	-18	4752	2672	35.5
	6	105.4	578	2624	27	1151	-16	6397	3668	44.5
30	2	29.1	236	1066	11	471	-10	2523	1428	18.4
	4	55.3	439	2075	10	844	-20	5153	3023	40.1
	6	88.2	675	2966	15	1060	-14	7676	4622	54.0
30	2	12.2	131	739	-3	357	-4	1799	1048	12.5
	4	31.3	365	1659	-8	777	-6	4169	2479	32.1
	6	56.8	644	2846	-6	1330	-9	7013	4110	53.4
31	2	22.4	150	714	-8	238	-13	1680	943	10.5
	4	45.6	338	1507	-3	650	-26	3756	2204	21.8
	6	90.4	564	2474	1	961	-37	6278	3713	41.8
31	2	12.7	122	618	-12	188	-6	1343	713	4.9
	4	33.4	276	1457	-17	553	-5	3224	1734	15.8
	6	66.5	422	2132	-23	735	-13	5041	2842	31.4
31	2	8.4	78	378	-2	144	-0	992	605	4.6
	4	25.5	181	749	-13	405	4	2291	1517	11.4
	6	62.5	355	1522	-13	612	2	4372	2787	29.5
32	2	-1.5	182	177	1	239	9	1189	1014	14.6
	4	-3.6	384	321	4	498	20	2255	1938	23.0
	6	-3.0	610	540	-2	777	40	3599	3062	33.4
32	2	-3.2	156	217	3	310	-4	857	644	5.9
	4	-4.2	382	376	-3	526	-5	1596	1224	8.9
	6	-1.7	638	612	-11	781	5	2852	2242	18.4
32	2	-2.9	207	177	-4	249	-6	1091	917	5.1
	4	-3.4	475	350	-7	450	-5	1807	1461	7.6
	6	-0.6	752	580	-9	781	3	2993	2414	16.7
33	2	-2.3	163	215	-12	302	3	933	720	6.3
	4	-2.9	395	393	-18	532	7	1904	1513	12.9
	6	2.5	646	705	-23	872	17	3057	2350	24.5
33	2	-1.0	226	226	-8	279	9	876	651	4.9
	4	-0.6	509	445	-12	581	15	1879	1435	11.2
	6	6.3	716	623	-14	944	20	3192	2563	28.9
33	2	-1.5	219	270	-8	287	-3	813	545	2.3
	4	0.8	549	517	-11	542	-1	1748	1230	11.6
	6	0.6	815	705	-20	872	2	2861	2156	24.7
34	2	0.2	205	220	-8	241	3	961	741	8.9
	4	-1.7	437	428	-15	500	7	2170	1744	19.4
	6	3.6	631	675	-21	821	8	3521	2843	34.2

APPENDIX C. Cumulative Yields of Leached Major Solutes (μeq/kg litter)

CODE	DAY	H	K	NH4	Cl	NO3	SO4	TotACY	WeakACY	TOC(mM)
34	2	1.5	236	241	-10	312	11	809	567	7.0
	4	1.3	433	391	-20	614	9	1524	1131	12.0
	6	8.2	576	675	-27	884	12	2728	2046	24.9
34	2	1.0	163	289	-9	270	9	916	626	7.8
	4	3.8	344	450	-19	485	5	1735	1281	13.1
	6	8.2	513	663	-27	847	11	2734	2063	24.5
35	2	-2.9	200	220	-6	276	9	1189	972	13.9
	4	-2.1	340	523	-16	492	13	2113	1592	22.0
	6	-3.0	528	863	-23	832	33	3207	2348	32.9
35	2	-0.4	236	232	-9	298	15	971	739	10.8
	4	-2.9	422	505	-16	633	23	1718	1215	13.5
	6	-4.8	648	832	-30	1007	30	2765	1937	23.6
35	2	-2.5	165	255	-8	314	12	1077	825	11.2
	4	-4.8	340	568	-23	583	24	1891	1327	24.7
	6	-4.8	557	923	-35	897	27	2861	1943	34.6
36	2	-1.7	182	175	-11	249	-4	914	741	11.6
	4	-2.7	390	382	-17	500	5	1609	1230	18.4
	6	-2.5	625	743	-19	794	21	3008	2267	32.9
36	2	-0.6	139	127	-13	207	3	1047	920	13.7
	4	-0.6	283	372	-21	409	7	1853	1481	16.7
	6	0.8	485	707	-25	678	14	3137	2429	30.2
36	2	0.8	158	84	-8	181	-6	781	697	4.4
	4	-1.5	338	357	-15	428	-3	1714	1358	14.4
	6	0.8	524	754	-19	618	1	3245	2490	29.5